

STUDIES OF
RECOMBINATION CENTERS IN SEMICONDUCTORS

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av

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STUDIES OF RECOMBINATION CENTERS IN SEMICONDUCTORS

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PER-OLOF FAGERSTRÖM



When I consider how my light is spent,...

(John Milton)

This thesis is based on experimental work carried out in the Department of Solid State Physics at Lund Institute of Technology. The results are published in five reports:

- I Photoconductivity of Zn-doped GaN (together with E Ejder)
- II Thermal and optical excitation processes in GaP:Cu
(together with H G Grimmeiss and H Titze)
- III Capture and thermal emission rates for electrons and holes
in Si:Pt (together with S Braun)
- IV TSC measurements and their correlation with photocurrent
techniques (together with H G Grimmeiss)
- V An alternative method of measuring photoionization cross
-sections in photoconductors.

Studies of Recombination centers in semiconductors

by

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Introduction

One of the major achievements of modern physics has been the success of solid state physics in creating new technologies.

Solid state physics constitutes a large branch of physics.

Semiconductor physics, one of the most important sub-fields

in solid state physics, cover the electrical, optical and

thermal properties and the interactions of all forms of

radiation in semiconductors. Some of these have been of interest since the 19th century, e g photoconductivity ¹⁾.

The physical properties of semiconductors can be considerably modified by the introduction of small amounts of foreign atoms.

In this manner, the resistivity of a silicon crystal can be changed by several orders of magnitude when silicon atoms in the crystal are replaced by suitable foreign atoms at concentrations of less than one part per million. Experimentally, it is found that replacing atoms of the host-lattice by foreign atoms alters the physical properties of the crystal in a way depending on the particular atoms introduced. Atoms belonging to a group of the periodic table adjacent to that of the semiconductor create

localized donors or acceptors in the otherwise forbidden energy gap. The properties of these shallow impurity levels, situated close to either the conduction band or to the valence band, are well understood ²⁻⁶).

Impurity levels which lie at a considerable distance from a band edge are called deep impurity levels. Although shallow impurities are used to determine the resistivity of the crystal and to determine if the current through the crystal is carried by electrons or holes, many important properties of semiconductors are determined or influenced by deep impurity centers. Although deep level impurities have been the subject of study for about twenty years, the field is still characterized by a lack of unambiguous experimental data and insufficient theoretical understanding. Recent reviews of the field ⁷⁻⁹) have underlined the fact that there is at present no general formalism available to predict the physical properties of these centers. Still it is possible to describe the usual processes where deep centers are involved.

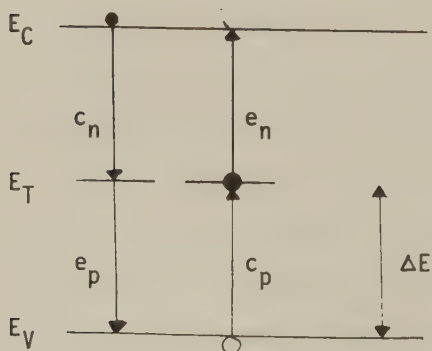


FIG.1

The four different processes illustrated in Fig 1 are the emission of electrons from the impurity level to the conduction band (e_n), the emission of holes from the level to the valence band (e_p), the capture of free electrons in the conduction band to the level (c_n) and the capture of free holes in the valence band to the level (c_p). The emission processes can be either thermally or optically induced. The capture (or recombination) of the free carriers can be radiative or non radiative. This means that a knowledge of eight different processes is needed to describe completely the properties of a particular impurity level.

Radiative recombination

Recombination processes which produce light have been intensively studied due to their technical importance. Within the last few years, the technology of light emitting diodes (LED) has been focused on making such improvements as extension of the range of the colours available and large segment displays in addition to the more obvious, higher efficiency and reliability and lower cost.

The possibility of extending the range of the colours of LED is dependent on the material used, since the energies of the photons emitted are less than the bandgap. Using GaP, this means that the wavelength of the light emitted is longer than 530 nm. GaN is a semiconductor with a direct bandgap of 3.5 eV. With such a wide bandgap, it is possible to extend the possible colours all over the visible spectrum into ultra violet. Impurities are often needed as activating centers for efficient luminescence. Usually capture of at least one type of carrier by these activators is a necessary

prerequisite for radiative recombination. It was soon established that GaN doped with Zn had strong blue and green photoluminescence ¹⁰⁾. At present no p-type GaN is available and since undoped GaN crystals are low ohmic, Zn was also interesting to study due to the fact that compensation to very high resistivity could be achieved by Zn ¹¹⁾. These were the reasons for the study of "Photoconductivity of Zn-doped GaN" (Paper 1). The study was carried out between 1971 and 1974, i.e. during the intensive years, when comprehensive research of GaN was carried out at the labs of RCA, Bell, General Electric Company (England) and at our department. From information about the Zn-level obtained in Paper 1, a simple calculation shows that, to get low ohmic p-type GaN, a very high concentration of Zn is needed. Using the Boltzman approximation, the concentrations of holes in the valence band (p) and of electrons in the Zn centers (n_T) can be described as

$$p = N_V \exp(-(E_F - E_V) / kT) \quad (1)$$

$$n_T = N_T \exp(-(E_T - E_F) / kT) \quad (2)$$

Here, N_V denotes the effective density of states in the valence band, N_T the total concentration of Zn-centers, E_F , E_V and E_T the energies of the fermi level, the edge of the valence band and the Zn-level respectively. From Paper 1, it is found that $E_T - E_V = 0.5$ eV. In order to get $p = 10^{16} \text{ cm}^{-3}$, $N_T > 5 \cdot 10^{21} \text{ cm}^{-3}$ even if we ignore such effects as increased selfcompensation which may be induced by high Zn-doping. As a final remark on GaN, it can be said that until the mechanism of the unintentional doping is known and until an impurity is found which introduces a shallow acceptor level, there is no application for GaN as a material for LED.

Killer centers

The importance of non-radiative recombination for LEDs can be expressed in terms of efficiency. The internal efficiency is the desired radiative recombination divided by the total recombination, i.e. the sum of radiative and non-radiative recombination. Though several hundred papers on the subject have been published ¹²⁾, many basic questions are still unanswered, or to quote A Haug ¹³⁾ "----- erfolgt strahlungslos; es bleibt dunkel. Mit diesen Eigenschaften hat leider auch die Theorie dieser Übergänge manches gemein -----".

In the III-V semiconductor materials, as well as in the II-VI, certain elements are known to introduce so-called "killer centers", i.e. centers with large capture cross sections for non-radiative recombination. Cu is such an element in GaP. Furthermore, it has been noticed that Cu enhances the degradation of LEDs ¹⁴⁾. As mentioned above, higher efficiencies and reliability are two major goals in research and development in the field of LEDs. For this reason, the properties of Cu-doped GaP were studied (Paper II). The two levels found in our work to be introduced by Cu-doping are called the A and B levels. The optical ionization energy of level A ($E_T - E_V \sim 0.7$ eV) is different in crystals with different shallow dopants. This is an interesting experimental result which requires more experiments to be carried out, to find a pattern so that the complex behaviour can be theoretically explained. Furthermore, for the first time a strong temperature dependence of the absolute magnitude of a photoionization cross section has been observed. From measurements of the thermal emission rate to the B center performed at different temperatures, the activation energy and the thermal capture cross section have been deduced. Due to the large hole capture cross section of the B level, a main recombination path in n-type

material will be through this level, even if the concentration of the centers is low. Since the luminescence of this recombination is in the far red, the efficiency of LEDs will decrease with Cu contamination.

Lifetime determining centers

The non-radiative recombination discussed above is not always unwanted and harmful. In Si-technology, deep impurity levels are introduced to control the lifetime of minority carriers. Different impurities are used or have been tested as lifetime controlling elements. To select the most suitable element for control of the lifetime in Si, detailed information is needed on several physical properties of the proposed impurities. To serve as an ideal lifetime controller, an impurity center should have the following properties:

- A: the ability to control the lifetime of minority carriers
- B: only give a minor contribution to the reverse current of pn junctions
- C: only give rise to a small recombination at high injection levels
- D: be easily and reproducibly incorporated into the semiconductor to a sufficient degree.

These demands can be quantified in terms of the solubility, diffusion constant, capture cross sections and binding energy of the impurity. To establish the criteria of an ideal lifetime controlling impurity, we will consider a n-type material.

The lifetime of holes is determined by

$$\tau_p^{-1} = \sigma_p \cdot v_p^t \cdot N_T \cdot f \quad (3)$$

where σ_p is the capture cross section for holes, v_p^t the thermal velocity of holes, N_T the total concentration of the electrically active impurity centers and f the fraction which is occupied by electrons. Since in an n-type material f equals unity when the center is below the fermi level, equation (3) reduces to

$$\tau_p^{-1} = v_p^t \sigma_p \cdot N_T \quad (4)$$

The contribution to the reverse-current of a pn junction from two step excitation is:

$$J_R = A \cdot \sigma_p \cdot v_p^t \cdot N_T \cdot N_V \cdot \exp(-\Delta E/kT) \cdot (1-f) \quad (5a)$$

or

$$J_R = A \sigma_n \cdot v_n^t N_C \exp(-(E_g - \Delta E)/kT) \cdot f \cdot N_T \quad (5b)$$

where A is a constant depending only on the geometry of the junction
5 a and b give together with

$$N_C N_V \exp(-E_g/kT) = n_i^2 \quad (6)$$

$$J_R = A \cdot n_i^2 N_T \sigma_p \cdot v_p \left(\frac{\sigma_p v_p}{\sigma_n v_n} N_V \cdot \exp(-\Delta E/kT) + \right. \quad (7)$$

$$\left. + N_C \exp((-E_g + \Delta E)/kT) \right)^{-1}$$

The recombination rate (R) at high injection levels is determined by electron and hole capture to the center, if excitation is neglected.

$$R = n \cdot v_n \cdot \sigma_n \cdot N_T \cdot (1 - f_2) = p \cdot v_p \cdot \sigma_p \cdot N_T \cdot f_2 \quad (8)$$

Since $p = n$ in high injection, it follows

$$R = p \cdot N_T v_p \cdot \sigma_p \cdot (\sigma_p v_p / (\sigma_n v_n) + 1)^{-1} \quad (9)$$

where p is the actual amount of injection.

From equation (4), it follows that, if the impurity center can be introduced in a sufficient concentration, any arbitrary lifetime can be achieved. To obtain a minor degree of compensation by the lifetime controller even at low concentrations of the shallow dopant, the capture cross section for minority carriers should be large. For certain values of lifetime, the values of J_R and R can be minimized. From equations (4), (6) and (7) it follows that

$$J_R = A n_i^2 \cdot \tau^{-1} \cdot \left(\frac{p_p v_p}{n v_n} N_V \exp(-\Delta E/kT) + N_C \exp(-E_g + \Delta E/kT) \right)^{-1} \quad (10)$$

ΔE or $E_g - \Delta E$ should be small so that J_R will be small, and other processes will dominate the reverse current.

(4) and (9) give:

$$R = p \cdot \tau^{-1} \cdot (\sigma_p v_p / (\sigma_n v_n) + 1)^{-1} \quad (11)$$

$$i.e. \sigma_p v_p \gg \sigma_n v_n$$

The limits of how close the levels can be to one of the bands and how large a ratio of $\sigma_p v_p / (\sigma_n v_n)$ can be used are set by the assumptions made, i.e. the level to act as a recombination center and not as a trap. This is equal to the condition that in neutral material the thermal excitation process between the level and the closest band is smaller than the recombination process between the level and the other band. A discussion similar to that above can be performed for p-type material.

The last criterion of an impurity (D) can be expressed as a sufficiently large solubility and a high diffusion constant for the impurity. If the impurity diffuses very rapidly into silicon (the semiconductor) the impurity can be diffused into manufactured devices without changing the p and n regions.

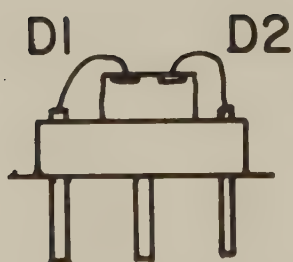
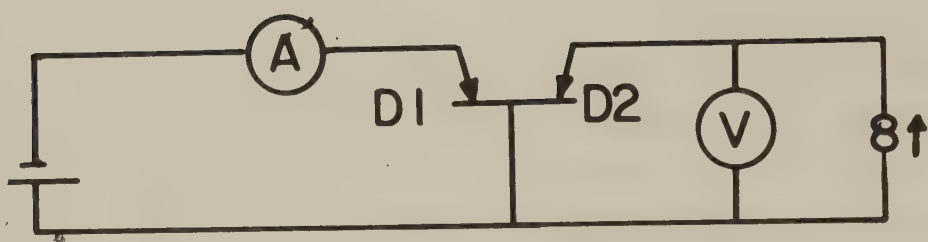
One element that has been proposed as a lifetime controlling center in Si is Pt. Due to the contradictory results published during the last years, the need for a detailed study was obvious. The analysis in Paper III of our own and previously published experimental results requires only the presence of two deep levels due to Pt doping of Si. The level at $E_C - 0.23$ eV is probably the one which controls the minority carrier lifetime.

In view of the data on different deep centers in silicon presently available, it can be stated that for applications in which the reverse-current of pn-junctions is essential, Pt might be a suitable dopant for the control of minority carrier lifetimes. On the other hand, if recombination must be small at high injection, which is equivalent to a large ratio of the lifetime at high injection to that at low injection, Au is better than Pt; Zn¹⁵⁾, however, seems to be even much more suitable than Au.

Measuring techniques

Due to the importance of recombination centers, it is essential in semiconductor technology to monitor the amount of deep centers desired and the absence of undesired centers.

In a recent review⁹⁾ of deep level impurities presented by H G Grimmeiss, the measuring techniques for characterizing deep levels



are summarized. Among the methods used, DLTS ¹⁶⁾ is a convenient method for automation and for routine measurements. To determine what impurity causes the signal, it is necessary to know the thermal emission rates as a function of temperature. As a result of our study of GaP:Cu (Paper II), it is possible to use DLTS to check if GaP is contaminated by Cu. Since TSC has also been proposed as a suitable routine-method for monitoring deep level impurities ¹⁷⁾, the GaP:Cu system was also investigated using the TSC-method (Paper IV). It is important to notice that although TSC is a simple experimental method it is inferior to DLTS. Though DLTS use a temperature scan, the result is independent of the heating rate. From an analysis of TSC, it is obvious that both the heating rate and the temperature in the space-charge region at the current peak must be known. A possible set-up for TSC experiments is shown in Fig 2. Diode 1 is used for the TSC measurement and diode 2 to monitor the temperature. Since the voltage in a forward-biased diode is linearly dependent on temperature at constant current, it is easy to obtain a conversion scale between voltage and temperature. If the photoionization cross section for a certain impurity is known, the optical properties of this center can be used to monitor its presence or absence. Since no sensitive method to measure photoionization cross sections in low ohmic bulk-material was available, such a method is described in Paper V.

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Thermal and optical excitation processes in GaP:Cu

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Abstrakt

The properties of two deep-level centers caused by Cu doping of GaP have been investigated in p^+n diodes and photoconductors by photocurrent methods. Spectra of the cross-sections for the optical transitions from the valence band to the impurity levels are presented. The bandgap energy and the threshold energy of the deeper level ($E_v + 0.7$ eV) have similar temperature dependences from 85 K to 300 K. A possible influence of other impurities on the optical threshold energy of this center is discussed. The absolute magnitude of the optical cross-section for excitation from the valence band to this deep level is temperature dependent. The thermal excitation from the valence band to the shallower level ($E_v + 0.5$ eV) is characterized by an activation energy of 0.55 eV, deduced from the temperature dependence of the thermal emission rate. A value of about $1 \cdot 10^{-13} \text{ cm}^2$ is estimated for the thermal hole capture cross section at 200 K.

Thermal and optical excitation processes in GaP:Cu

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Introduction

In general, elements which replace an atom of the host-lattice create deep impurity levels if they do not belong to those groups of the periodic table adjacent to that (those) of the semiconductor. A negative (but important) reason for the current interest in deep impurities is that they affect carrier lifetimes even when present in concentrations so small that separate experiments for impurity identification have little chance of success. Other (sometimes harmful) effects include non-radiative recombination processes which can affect the efficiency of light emitting diodes. However, deep level impurities may also give rise to desirable effects in devices. The high quantum gains of photoconductors are usually obtained by just these centers. Although deep level impurities have been studied for about 20 years, this is one of the fields still characterized by a lack of unambiguous experimental data and insufficient theoretical understanding. In many cases, even the most simple information about the properties of deep centers is not available. Sometimes this is due to a complex behaviour of the impurity. Copper in GaP is one such example.

Although the optical and electrical properties of Cu-doped GaP have been studied previously¹⁻¹², there is still to be found in the literature considerable disagreement among the values for the energy-positions of the centers originating from copper. In most of the earlier work¹⁻⁸, static and dynamic photoconductive properties have been investigated, the energy positions of centers involving copper impurities being often deduced from measured values of the threshold energies for photoconductivity quenching and stimulation. Due to the lack of any detailed analysis, these values have often been estimated and are therefore sub-

ject to errors. Later, more detailed investigations were performed using absorption ⁹⁾, luminescence ¹⁰⁾, photoquenching of luminescence ¹¹⁾ and thermally-stimulated current measurements ¹²⁾.

The results are summarized in Table 1. Although the values for the energy positions obtained differ considerably in some cases, they can be classified rather well into two groups with energies of about 0.52 eV (A-center) and 0.7 eV (B-center). In addition, some authors report the presence of an energy level at about 0.64 eV. However, this energy level is also seen in GaP samples not intentionally doped with copper and is therefore not considered here. In a previous work ¹³⁾, complex behaviour of copper in GaP was already reported, a number of complex centers with lattice defects and other impurities having been observed.

In this paper, detailed data on optical emission rates in copper doped GaP as a function of photon energy obtained at different temperatures using different techniques of investigations are presented. Two centers have been detected. The temperature dependence of the optical threshold energy of one centre has been investigated. Thermal emission rates have been measured using optically-induced dark-current transients, the value of the thermal activation energy obtained being compared with optical threshold energies. Furthermore, a possible influence of other impurities on the optical threshold energy of centres involving copper is reported.

II. Experimental details

The starting material for producing copper doped samples for measurements of photoconductivity was sulfur-doped n-type GaP substrates with a free carrier concentration between 10^{17} - 10^{18} cm⁻³ at room temperature. These substrates were first metallized with copper by surface diffusion at a temperature of about 400° C in an evacuated quartz ampoule ³⁾ and then heated for about 12 hours in a second ampoule at temperatures between 600 and 750° C (sample 001).

p⁺n diodes were prepared by diffusing copper in Sn-doped LPE layers on lightly S-doped GaP substrates (sample 227 and 237). The n-type copper-doped layers were then diffused with zinc for 20 minutes

Reference	$E_T - E_V$ (eV)		Temperature
	A	B	
Allen and Cherry (Ref 1)		0.68	300
Nasledov and Slobodchikov (Ref 2)	0.55		290
Grimmeiss and Koelmans (Ref 4)	~0.55	~0.7	300
Goldstein and Perlman (Ref 5)	0.55	0.7	77, 300
Grimmeiss and Olofsson (Ref 7)	0.55	~0.75	298
Grimmeiss and Ottosson (Ref 8)	~0.55	~0.7	300
Olsson (Ref 9)		0.7	300
Monemar (Ref 10)	0.5-0.55	~0.7	4
Grimmeiss and Monemar (Ref 11)	0.51		77
Fabre and Bhargava (Ref 12)	0.54		

Table 1

at 800° C using Zn-Ga alloy. Reference diodes were prepared using the same method without, however, intentionally diffusing copper (sample 207). In some cases, p⁺n junctions were prepared by diffusing zinc in copper doped n-type GaP samples ¹⁴⁾, the starting material of which had earlier been doped with Te (sample 302).

Spectral distributions of cross sections were measured using a Zeiss MM12 double prism monochromator. In those cases in which high intensities were needed, a Bausch & Lomb high intensity grating monochromator or a Coherent Radiation CR12 Argon laser in conjunction with a CR590 dye laser was employed. Relative intensities were monitored using a thermocouple and a lock-in amplifier. Absolute values were measured using a pyroelectric detector. DC current measurements were performed with a Keithley electrometer 616 or 602. For most of the transient photocurrent measurements, a Keithley 427 current amplifier was used.

III. Photoionization cross section of holes.

In diodes which had not intentionally been doped with copper, only one deep level center was observed using the photocurrent technique ¹⁵⁾. From the spectral distribution of the photoionization cross section (fig 1), an optical threshold energy of about 0.62 eV can be deduced. The maximum value of the photoionization cross section is about $2 \cdot 10^{-17} \text{ cm}^2$. Using photocurrent transient measurements, the total concentration of electrically-active deep-level centers was estimated to be less than $5 \cdot 10^{12} \text{ cm}^{-3}$.

After diffusion of copper two other centers (A- and B-centers), different from the mentioned above were observed. The sum of their concentrations was typically larger than $5 \cdot 10^{13} \text{ cm}^{-3}$. From photocapacitance measurements, it follows that both centers lie in the lower half of the bandgap. Measurements of the spectrum for exciting electrons from the valence band to the deep centers were made using photocurrent transients techniques at

temperatures at which the thermal emission rates could be neglected. Initially, the p^+n diode being investigated was reverse biased and illuminated with light of photon energy $h\nu$ greater than ΔE_{nA}^0 (see fig 2). When this light is removed, some of the A and B centers are empty. If thermal excitation processes can be neglected, the hole occupancies of the centers, $p_A(0)$ and $p_B(0)$, are not changed when the light is removed. Photons of energy $h\nu_s$ greater than ΔE_{pA}^0 but less than ΔE_{pB}^0 refill only the A-center, resulting in a transient photocurrent given by ¹⁷⁾

$$J_{TT}^0(t) = \frac{1}{D} q A (W - W_0) e_{pA}^0 p_A(0) \exp(-e_{pA}^0 t). \quad (1)$$

where D is a factor depending on the experimental conditions, A is the junction area, W is the depletion-layer width and W_0 is the width of that part of the depletion layer which is inoperative in the optical emission rate of holes ¹⁵⁾. The time constant of the transient photocurrent is thus $(e_{pA}^0)^{-1} = (\sigma_{pA}^0 \phi)^{-1}$ where σ^0 is the optical cross section and ϕ is the photon flux.

For experimental reasons (e.g., to eliminate noise at very low current levels), it is sometimes advantageous to integrate the photocurrent with respect to time, which gives the charge Q flowing in the external circuit when the centers are refilled. From eqn 1, the charge Q can be calculated to be

$$\begin{aligned} Q(t) &= \int J_{TT}^0(t) dt = \frac{1}{D} q A (W - W_0) p_A(0) [1 - \exp(-e_{pA}^0 t)] = \\ &= Q_\infty [1 - \exp(-e_{pA}^0 t)] \end{aligned} \quad (2)$$

The time constant and relative photon flux are determined as functions of photon energy $h\nu_s$ and hence a spectrum of σ_{pB}^0 is determined in a similar way. However, in this case, after removing the light of photon energy $h\nu_p$ the A-centers were filled first and then the B-centers (fig 3). Absolute values of σ_{pA}^0 and σ_{pB}^0 were obtained by making a measurement of the absolute magnitude of the photon flux at $h\nu = 1.03$ eV. For these measurements, good exponential photocurrent decays were obtained (fig 4). The presence of two deep energy levels is readily demonstrated by plotting Q_∞ versus $h\nu_s$. In this case, Q_∞ has been measured

by initially shining light of a constant photon energy $h\nu_p$ greater than ΔE_{pA}^0 on the diode and then integrating the total photocurrent transient obtained due to the illumination with photons of energy $h\nu_s < \Delta E_{nB}^0$. Because $h\nu_p$ is constant, Q_∞ will change for every additional deep center which is recharged by shining light of energy $h\nu_s$ on the sample. Figure 5 clearly shows that two steps with threshold energies of about 0.5 eV and 0.7 eV are observed, in agreement with the results obtained from the spectra of σ_{pA}^0 and σ_{pB}^0 (figure 3). Similar results were obtained at 200 K and 300 K.

No field dependence of σ_{pA}^0 and σ_{pB}^0 was observed when the maximum electric field in the space charge region of the diode was changed by a factor of about 3. This results is in agreement with measurements of the optical quenching of photoconductivity. The technique used has been described previously¹⁸⁾. Because the electric field is small in photoconductors, any field dependence up to about 10^5 V/cm should be observed by comparing the spectra of σ_{pA}^0 and σ_{pB}^0 obtained in bulk photoconductors and diodes. Fig 6 shows that within the experimental error the spectral distributions are not affected by electric fields. Using both measurement techniques, the spectrum of σ_{pB}^0 was also investigated at 200 K (fig 7) and 300 K (fig 8). Because transient measurements are less straightforward than steady-state measurements, the increase in the photocurrent Δj_R^0 due to illumination with a second light source of constant photoenergy 2.05 eV and high intensity was also investigated at 300 K¹⁵⁾. Once again, within the experimental errors, similar spectra are obtained with different measuring techniques. Already at 200 K thermal excitation processes can no longer be neglected for the A-center, which makes an unambiguous analysis of the experimental data difficult. It is obvious from the results presented in figs 6, 7 and 8 that the spectral distribution of σ_{pB}^0 is dependent on temperature. To demonstrate that there is no thermal broadening of the impurity absorption edge within the experimental error for all three temperatures, the

curves obtained at 85 K and 200 K have been normalized to the 300 K data (fig 9). This has been carried out by shifting the curves to lower energies by 35 meV at 200 K and 60 meV at 85 K. A comparison of the temperature dependence of ΔE_{pB}^0 with that of the energy bandgap¹⁹⁾ indicates that in both cases a similar temperature dependence exists. The absolute value of σ_{pB}^0 increases by almost a factor of 8 when the temperature is raised from 85 K to 300 K.

The cross sections σ_{nA}^0 and σ_{nB}^0 for the photoionization of electrons from the deep centers to the conduction band are normally determined by using a transient photocapacitance technique¹⁷⁾. However, all our GaP diodes showed irregularities with respect to photocapacitance. To get at least some information about the threshold energy, the hole occupancy p_B of the B-centers was determined using the transient photocurrent technique. From eqn 1, it follows that the initial photocurrent $J_{TT}^0(0)$ is proportional to the hole occupancy if the intensities and energies of the photons $h\nu_s$ used to refill the B-centers are kept constant. Neglecting recombination in the space charge region, the hole occupancy $p_B(0)$ of the B-centers due to light of photon energy $h\nu_p$ larger than ΔE_{nB}^0 but less than ΔE_{nA}^0 is given by

$$p_B(0) = \frac{e_{nB}^0}{e_{nB}^0 + e_{pB}^0} N_{TTB} \quad (3)$$

where e_{nB}^0 and e_{pB}^0 are the optical emission rates for photon energies $h\nu_p$ and N_{TTB} is the concentration of B-centers. Because e_{pB}^0 is rather constant at these photon energies, it might be assumed that $p_B(0)$ is proportional to e_{nB}^0 as long as $e_{nB}^0 \ll e_{pB}^0$. Although $h\nu_p$ was smaller than ΔE_{nA}^0 for these investigations, it turned out for the A-centers that a considerable hole occupancy, due to illumination with photons of energy $h\nu_p$ was created. Hence, after the light of photon energy $h\nu_p$ was removed, the diode was first illuminated with photon energy $\Delta E_{pA}^0 < h\nu < \Delta E_{pB}^0$ to refill the A-centers before $p_B(0)$ was determined. From the

spectral distribution of $p_B(0)$ (fig 10), an optical threshold energy of about 1.55 eV is found. A similar threshold energy is obtained for $p_A(0)$ probably due to the recapture of holes which have been generated by the excitation of electrons from the valence band to the B-centre.

The experiments so far described were performed on copper-doped GaP, the starting material of which was Sn-doped GaP. It has been observed previously ¹³⁾ that copper in GaP forms a large number of complex centers with lattice defects and other impurities. To determine whether or not the shallow background doping has any influence on the spectral distribution of σ_A^0 and σ_B^0 , samples with different background doping were investigated. Figure 11 shows the spectral distribution of σ_{pB}^0 at 200 K and 300 K for a photoconducting sample, the starting material of which was sulfur-doped GaP. The 200 K curve is shifted 35 meV to lower energies in order to demonstrate that the curve form is the same for both temperatures. Comparing these data with those presented in fig 9, it is readily seen that the threshold energy of the sulfur-doped GaP:Cu sample is about 35 meV larger. This shift is clearly larger than the experimental error.

Fig 12 shows the spectral distribution of σ_{pB}^0 obtained from photocurrent transient measurements at 300 K and 85 K in p^+n diodes in which the n region is doped with Te ¹⁴⁾. The curves are normalized by shifting the 85 K curve 60 meV to lower energies. The threshold energy of the Te-doped sample is about 20 meV smaller than the value obtained for the Sn-doped samples. Plotting the spectral distribution of σ_{pB}^0 at 300 K for the Sn-, Te- and S-doped samples, respectively, by shifting the Te data 20 meV to higher energies and the S data 35 meV to lower energies, it is easily seen that in all three cases the same curve form is obtained (fig 13). If the A and B-centers were coupled, a similar shift in threshold energy should be observed for σ_{pA}^0 . Fig 14 shows however, that the spectral distributions of σ_{pA}^0 for the Sn-, S- and Te-doped samples are the same within the experimental error.

IV. Thermal emission rates

It has already been mentioned that above about 150 K thermal excitation processes from the valence band into the A-centers can no longer be neglected. On the other hand, this behaviour can be used to measure the thermal activation energy of the A-centers. For these measurements, sample 227 was illuminated with photons of energy 2.05 eV resulting in changes of occupancy in both the A- and the B-centers. Due to the thermal refilling, the concentration of empty A-centers will change after the light source is removed, at a rate given by

$$\frac{dp_A}{dt} = e_{nA}^t (N_{TTA} - p_A) - e_{pA}^t p_A, \quad (4)$$

where e_{nA}^t and e_{pA}^t are the thermal emission rates of electrons and holes, respectively. Because for the A-centers $e_{pA}^t \gg e_{nA}^t$, the time dependence of the density of empty A-centers is given by

$$p_A(t) = p_A^i(0) \exp(-e_{pA}^t t) \quad (5)$$

where

$$p_A^i(0) = \frac{e_{nA}^o}{e_{pA}^o + e_{nA}^o + e_{pA}^t} N_{TTA} \quad (6)$$

The thermally stimulated current due to the refilling of empty A-centers after the light source is removed is proportional to $p_A(t)$ with a time constant of $(e_{pA}^t)^{-1}$. Performing these measurements at different temperatures thus gives information on the temperature dependence of the thermal hole emission rate e_{pA}^t which is related to the thermal hole capture cross section σ_{pA} by detailed balance:

$$e_{pA}^t = g^{-1} \sigma_{pA}^t v_{th} N_v \exp(-\Delta E_{pA}^t/kT) \quad (7)$$

Here g is the degeneracy factor of the A-centre, v_{th} is the mean thermal velocity of holes, N_v is the valence band effective density of states and ΔE_{pA}^t is the thermal activation energy at the temperature of measurements. The temperature dependence of σ_{pA}^t is not known. However, assuming $\sigma_{pA}^t \sim T^{-2}$ because the A-center is probably an attractive centre, a thermal activation energy ΔE_{po}^t can be estimated by plotting the logarithm of σ_{pA}^t against T^{-1} (fig 15). A value of 0.547 ± 0.02 eV for ΔE_{po}^t is obtained if g is taken as unity. The observation that ΔE_{po}^t is larger than ΔE_{pA}^o is attributed to the fact that ΔE_{pA}^o refers to the temperature of measurements whereas ΔE_{po}^t is the linearly extrapolated absolute zero energy value. The temperature dependence of ΔE_{pA}^o could not be measured in our samples. However, if a similar temperature dependence for the A-center is assumed¹¹⁾ as for the B-center a value of about 0.54 eV for ΔE_{po}^t can be expected for the temperature range in which the measurements were performed. Neglecting any Franck-Condon shift and, hence, taking $\Delta E_{pA}^t = \Delta E_{pA}^o = 0.5$ eV a value of about $1 \cdot 10^{-13} \text{ cm}^2$ for σ_{pA}^t is estimated at 200 K using Eq 7 and the data presented in fig 15.

V. Discussion

The results presented in Fig 1 and Fig 3 indicate that copper is probably responsible for both the A and B centers. However, the fact that the threshold energy of the B-center depends on the shallow background doping probably means that at least for the B-center copper forms some kind of complex. This might on the one hand explain why the maximum photoionization cross section σ_{pB}^o is temperature dependent. To the best of our knowledge, such a strong dependence of an optical ionization cross section on temperature has not hitherto been observed. On the other hand, the forming of complexes due to different background doping might be the reason for the considerable disagreement in published values for the energy position of the B-center. In fig 16 a normalized plot of optical data is shown for published values of the excitation of electrons from the valence band into the B-center. It is interesting to note that the starting material in ref 4 and 8 was probably sulfur doped as was sample 001 in this paper. Furthermore, the data obtained with our Te-doped samples are close to the results of ref 1 and ref 5. Thus, the discrepancies in the published values of the energy positions

in GaP:Cu is mostly due to the methods of analysis used and to a some previously unobserved influence of other impurities rather than to inconsistencies in the experimental data. This might suggest that the B-center is a complex between copper and shallow impurities although further work must be performed to prove this.

No evidence could be found that the A and B centers are coupled. On the contrary, measurements indicate that the concentrations of the centers are independent of each other. The closeness of the thermal and optical activation energy ΔE_{pA} suggests that the Franck-Condon shift is small. This is probably also valid for the B-center because the sum of the optical activation energies $\Delta E_{pB}^0 + \Delta E_{nB}^0$ is about 2.31 eV at 85 K, which value does not differ greatly from the bandgap energy of GaP¹⁹⁾ (2.33 eV).

In a previous paper¹¹⁾, a deep level in GaP:Cu with a threshold energy of about 0.51 eV was investigated using the photoluminescence quenching technique. The good agreement between these data and the results presented in this paper (Fig 14) suggests that in both cases the same impurity center has been investigated. To make sure that the differences in optical threshold energies in samples with different shallow impurity dopings are not due to experimental errors, the spectral distribution of σ_{pB}^0 was carefully measured in two diodes which were both doped with Sn but prepared from two different LPE layers (sample 227 and 237). Within the experimental error, no difference in the spectra could be observed.

In most analyses of photocurrent and photocapacitance measurements, it is assumed that recombination and in particular "recapture" processes can be neglected. It has already been pointed out in a previous paper¹⁸⁾ and confirmed by the investigations presented in this paper that recapture and probably also recombination processes may be important within the spacecharge region of a junction barrier when the occupancy of deep energy levels is changed due to optical excitation. For these processes to occur, the thermal capture cross section must be large. The large capture cross section estimated from the thermal emission rate e_{pA}^t by detailed balance might well explain the rather strong capture of

free holes by the A-centers.

No attempt has been made to determine the energy positions of the A- and B-centers more accurately. The easiest way to do this would have been to compare the experimental data with calculated photo-ionization cross sections. However, at present no accurate information about the density of states in the valence band of GaP is available. This makes calculations from data at temperatures above 85 K rather uncertain. The threshold energies given in this paper have therefore been estimated from the Lucovsky model²⁰⁾.

VI. Conclusions

The measurements outlined in this paper indicate that at least two deeplying energy levels are caused by doping GaP with copper. One of the particular centers investigated here, the B-center, has interesting properties. It has an optical threshold energy, which is probably influenced by the presence of other impurities. The sum of the electron and hole ionization energies of this center is close to the bandgap energy indicating a small value for the Franck-Condon shift. The temperature-dependence of ΔE_{pB}^0 is similar to that of the bandgap. Similar results have been obtained for ΔE_{pA}^0 in a previous paper¹¹⁾. The thermal activation energy ΔE_{pA}^t determined from the temperature-dependence of the thermal emission rate e_{pA}^t is in good agreement with ΔE_{pA}^0 suggesting that also for the A-center the Franck-Condon shift may be small. Hole capture processes observed in the space charge region of the diodes are explained by the relatively large thermal capture cross sections estimated by detailed balance.

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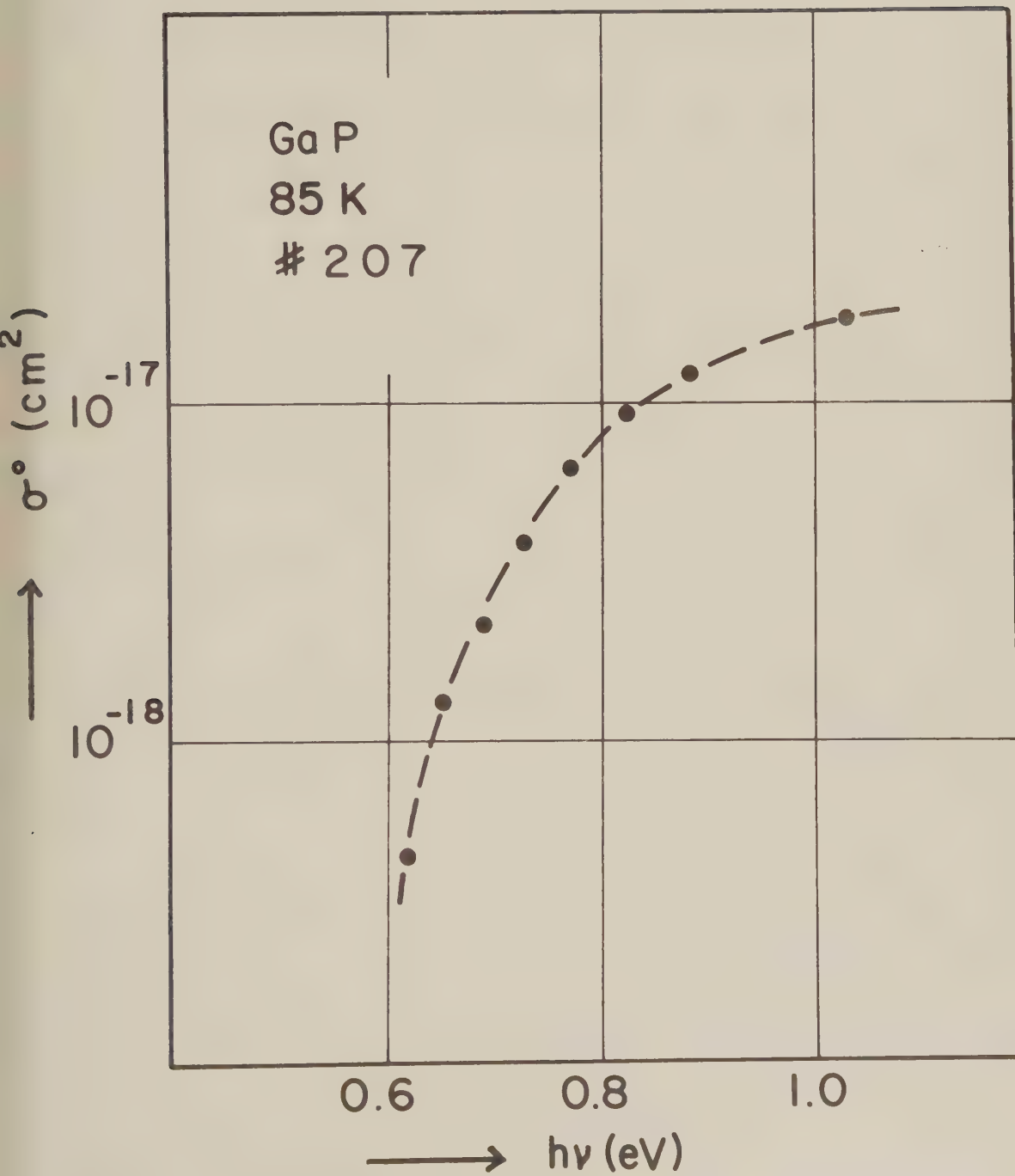
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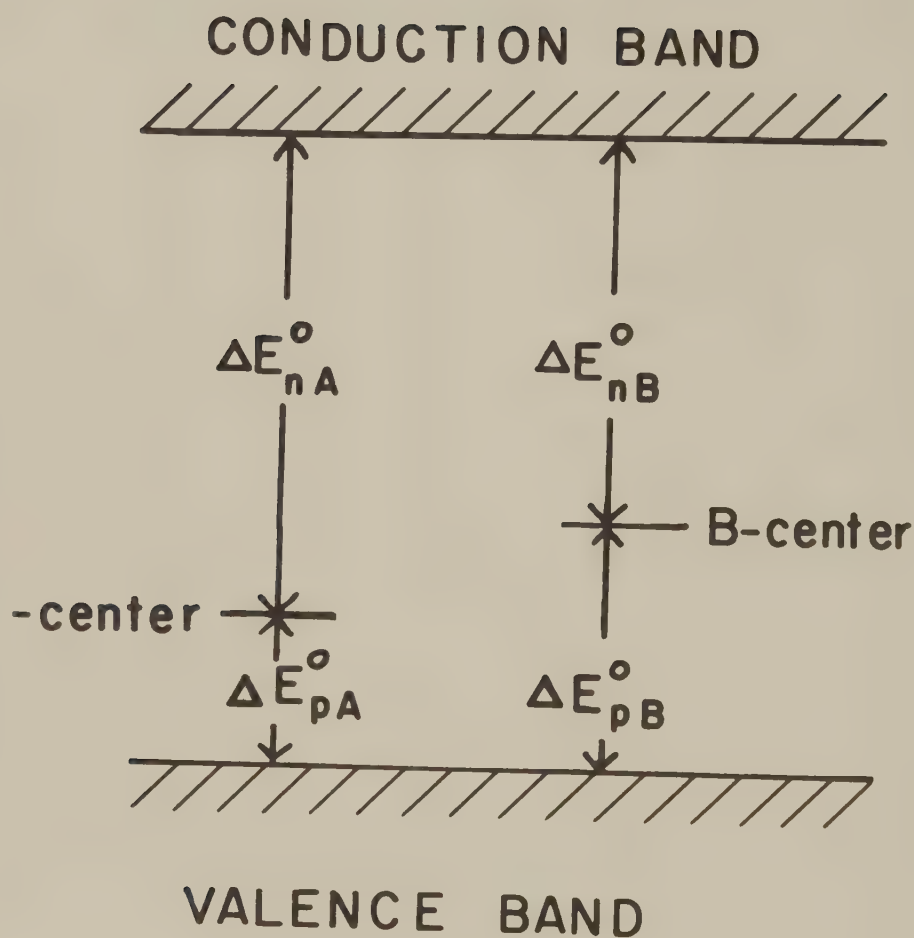
- Fig 1 Spectral distribution of the absolute photoionization cross section σ^0 at 85 K in GaP p^+n diodes without intentional Cu:doping.
- Fig 2 Diagram illustrating energy differences.
- Fig 3 Spectrum of the photoionization cross sections σ_{pA}^0 and σ_{pB}^0 in copper doped GaP at 85 K as determined by photocurrent transients. The solid curves are photoionization cross sections calculated using the Lucovsky model ²⁰⁾ with threshold energies 0.51 eV and 0.72 eV, respectively.
- Fig 4 A typical plot of the decay of the photocurrent due to the refilling of B-centers by optical transitions from the valence band. The diode has zero bias at 85 K and the photon energy of the exciting light is 1 eV.
- Fig 5 The integrated charge Q_∞ associated with refilling centers by optical transitions from the valence band as a function of the excitation photon energy. The GaP diode has zero bias at 85 K.
- Fig 6 Spectrum of the sum $\sigma_{pA}^0 + \sigma_{pB}^0$ at 85 K as determined by optical quenching of the photoconductivity (o). The full circles (●) are the differences between the experimental data (o) and the dotted curve which has been calculated using Lucovsky's modes ²⁰⁾ with threshold energy 0.51 eV. For comparison, the data for σ_{pB}^0 of Fig 3 are also shown (Δ).
- Fig 7 Spectrum of the photoionization cross section σ_{pB}^0 at 200 K as determined by optical quenching of photoconductivity ¹⁸⁾ (o) (sample 3536) and photocurrent transient technique (o) (sample 227).

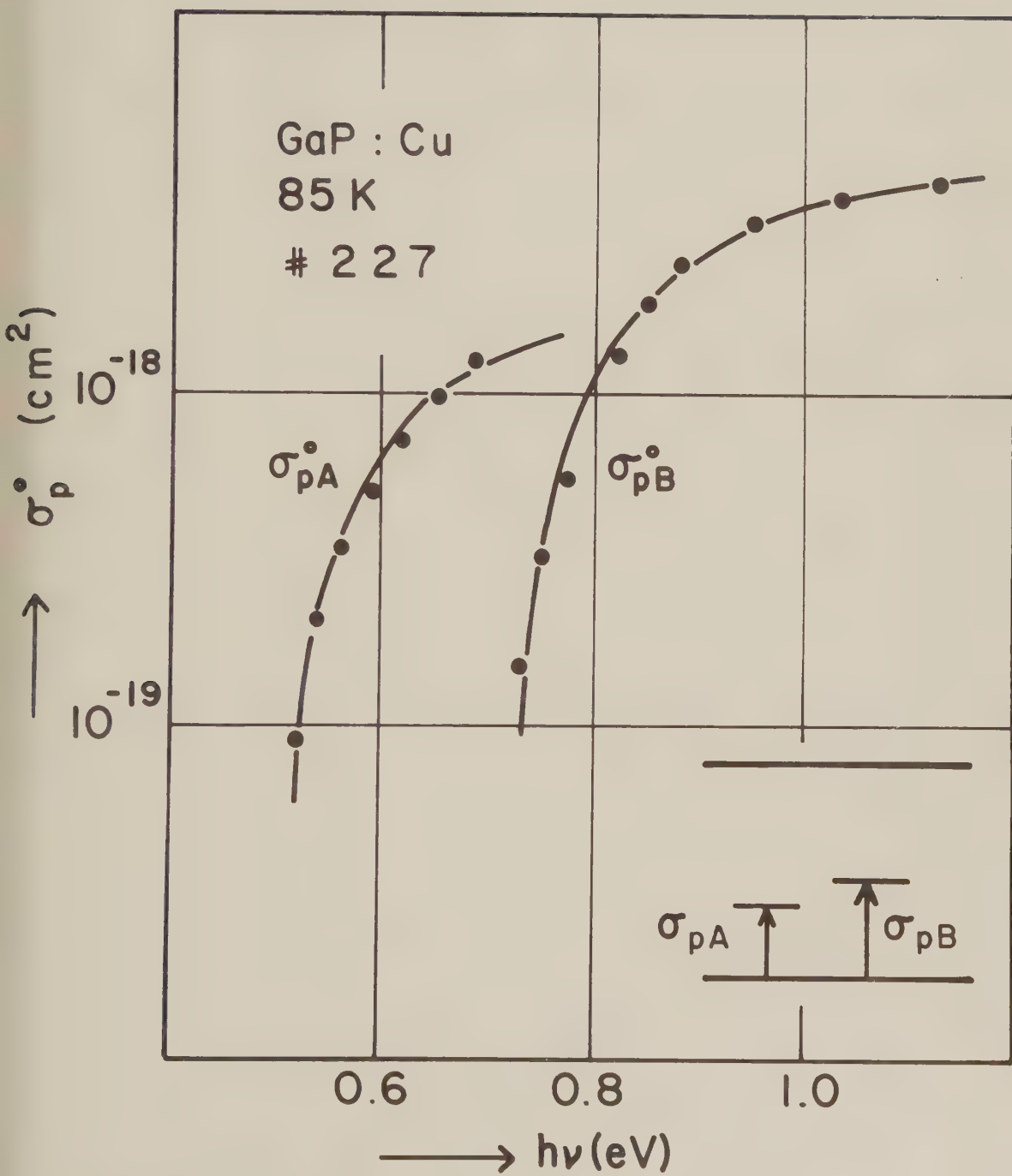
- Fig 8 Spectrum of the photoionization cross section σ_{pB}^0 at 300 K as determined by the constant photconductivity respons technique (o) (sample 3536), the increase in the photocurrent ΔJ_R^0 ¹⁵⁾ (Δ) (sample 227) and photocurrent transient technique (o) (sample 227).
- Fig 9 Normalized spectral distributions of σ_{pB}^0 at different temperatures. Compared with the 300 K (●) values, the energy scales for the 85 K (Δ) and 200 K (o) values are shifted to higher energies by 60 and 35 meV, respectively.
- Fig 10 Logarithm of the hole occupancy p_B as a function of the excitation photon energy $h\nu$ at 85 K.
- Fig 11 Normalized spectral distributions of σ_{pB}^0 at 200 K (o) and 300 K (●) as determined by optical quenching of photoconductivity (sample 001). The energy scale for the 200 K values is shifted to higher energies by 35 meV.
- Fig 12 Normalized spectral distributions of σ_{pB}^0 at 85 K (o) and 300 K (Δ) as determined using the photocurrent transient technique (sample 302). The energy scale for the measurement at 85 K is shifted to higher energies by 60 meV. For comparison, calculated photoionization cross sections using the Lucovsky model²⁰⁾ with threshold energy 0.67 eV are also shown (---).
- Fig 13 Normalized spectral distribution of σ_{pB}^0 at 300 K for samples with different shallow background doping. Compared with the values of the Sn-doped sample 227, the energy scales for the Te-doped sample 302 (o) and the S-doped sample 001 ($\blacktriangle$) are shifted by 20 meV to higher and 35 meV to lower energies.
- Fig 14 Spectrum of the photoionization cross section σ_{pA}^0 at 85 K as determined by optical quenching of the photconductivity (Δ sample 001), photocurrent transient technique (● sample 302, o sample 227) and optical quenching of photoluminescence¹¹⁾ (+).

Fig 15 Variation with temperature of the rate of thermal excitation of electrons from the valence band into the A-centers, plotted as e_{pA}^t versus T^{-1} .

Fig 16 Comparison of published data for σ_{pB}^0 with results presented in this paper at 300 K. (O) ref 1, (Δ) ref 5, (x) ref 4, ($\bullet$) ref 8, (--) S doped GaP (sample 001), (—) Te doped GaP (sample 302).







→ $Q_{\infty} - Q(t)$ (A.U)

10

1

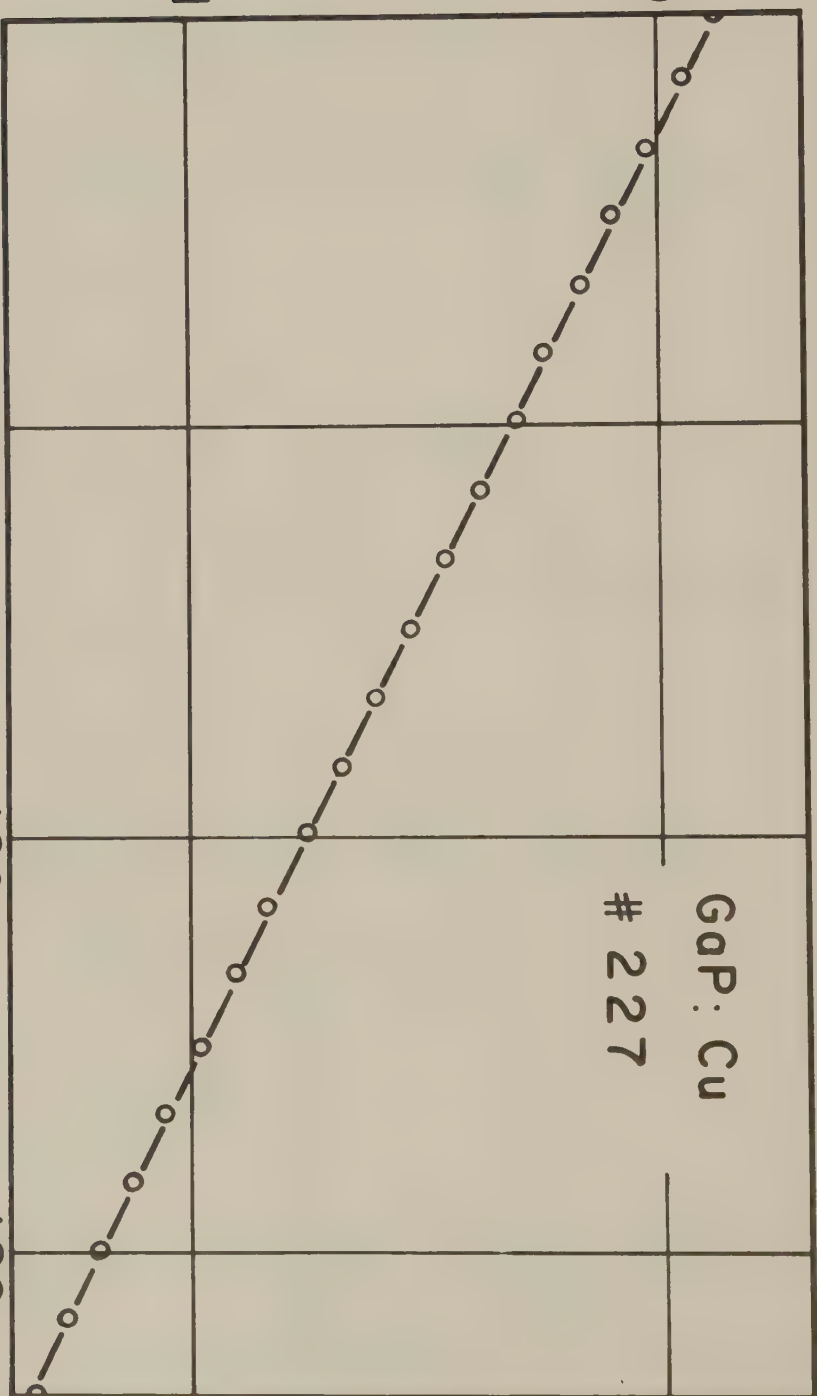
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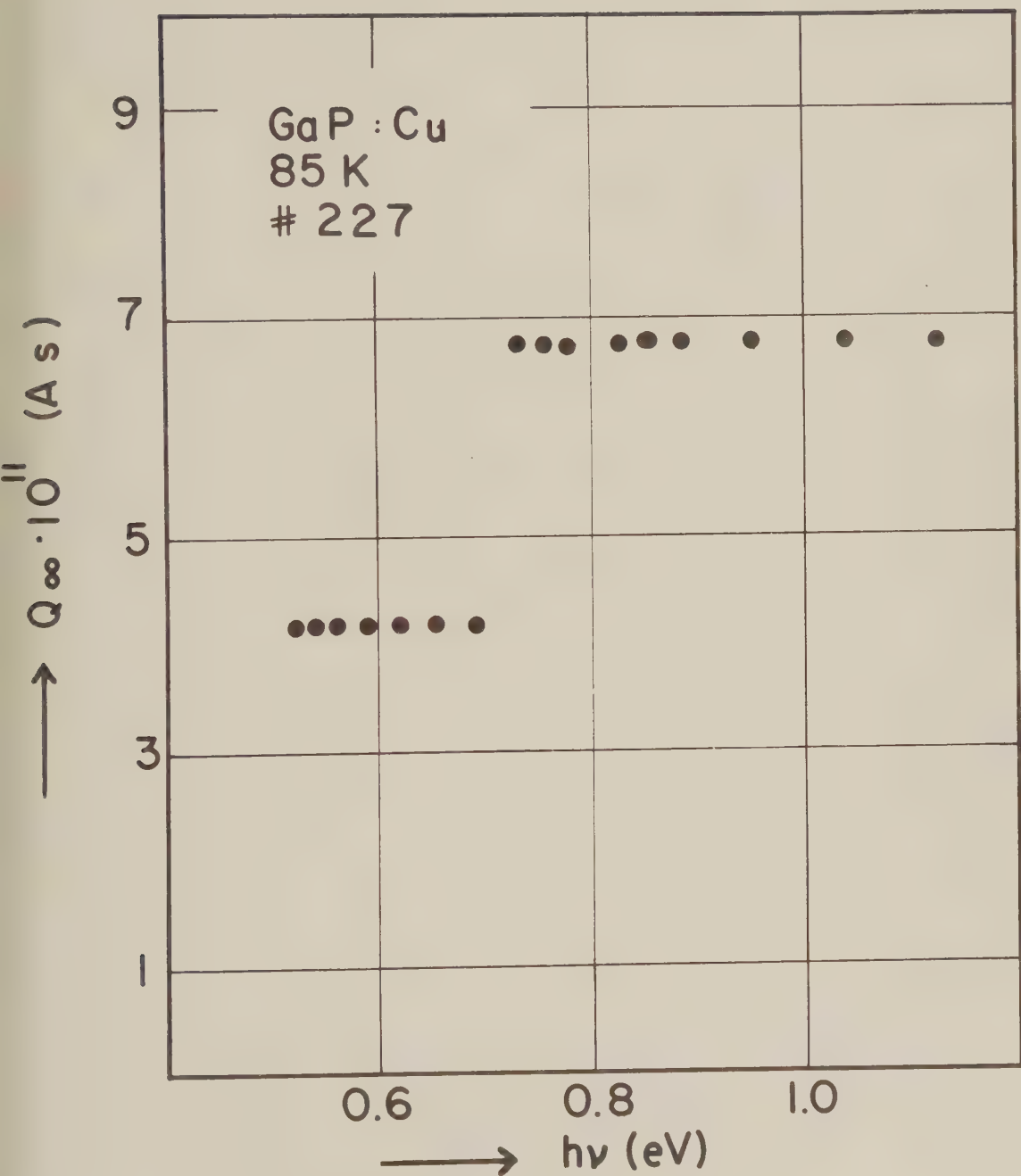
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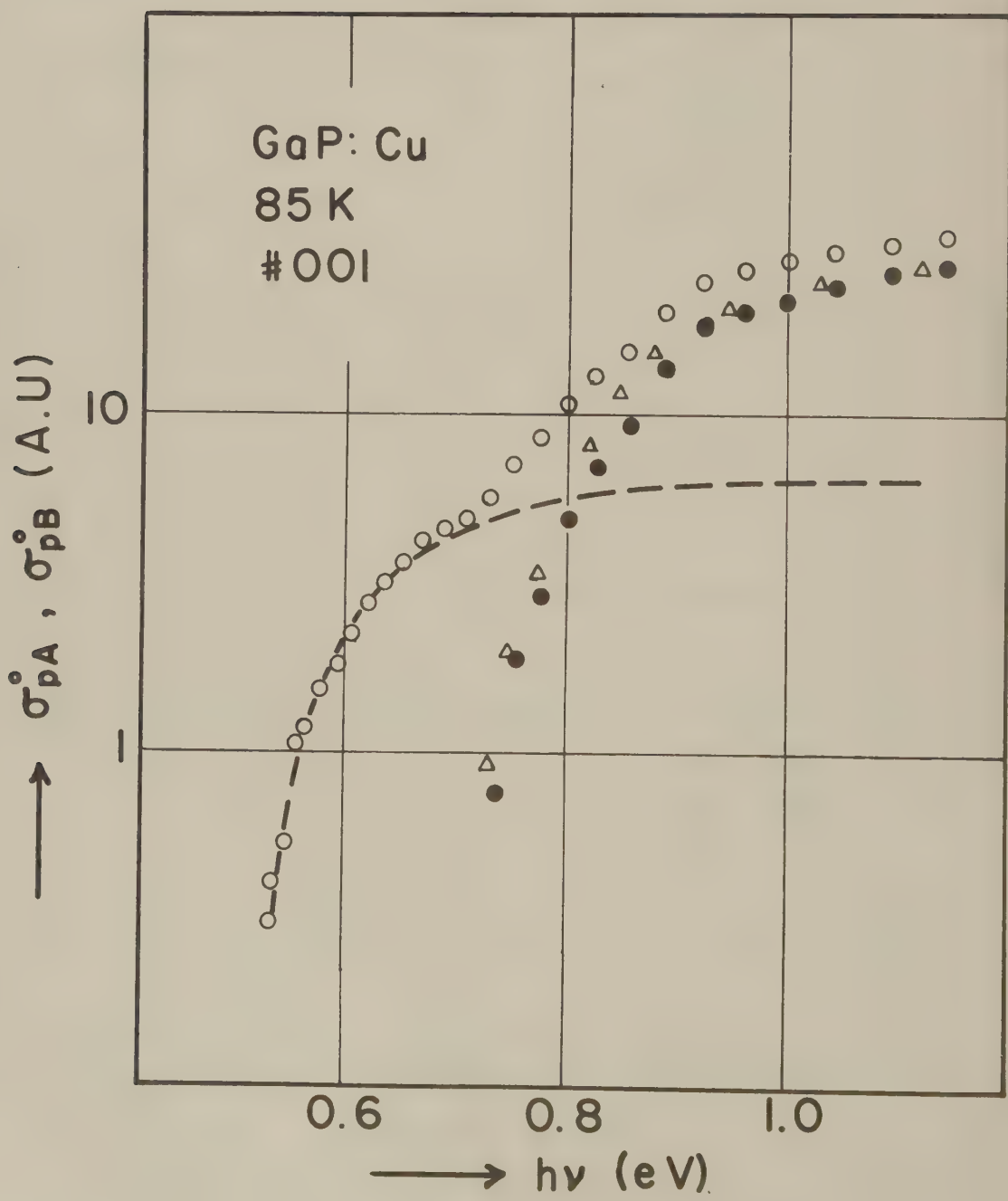
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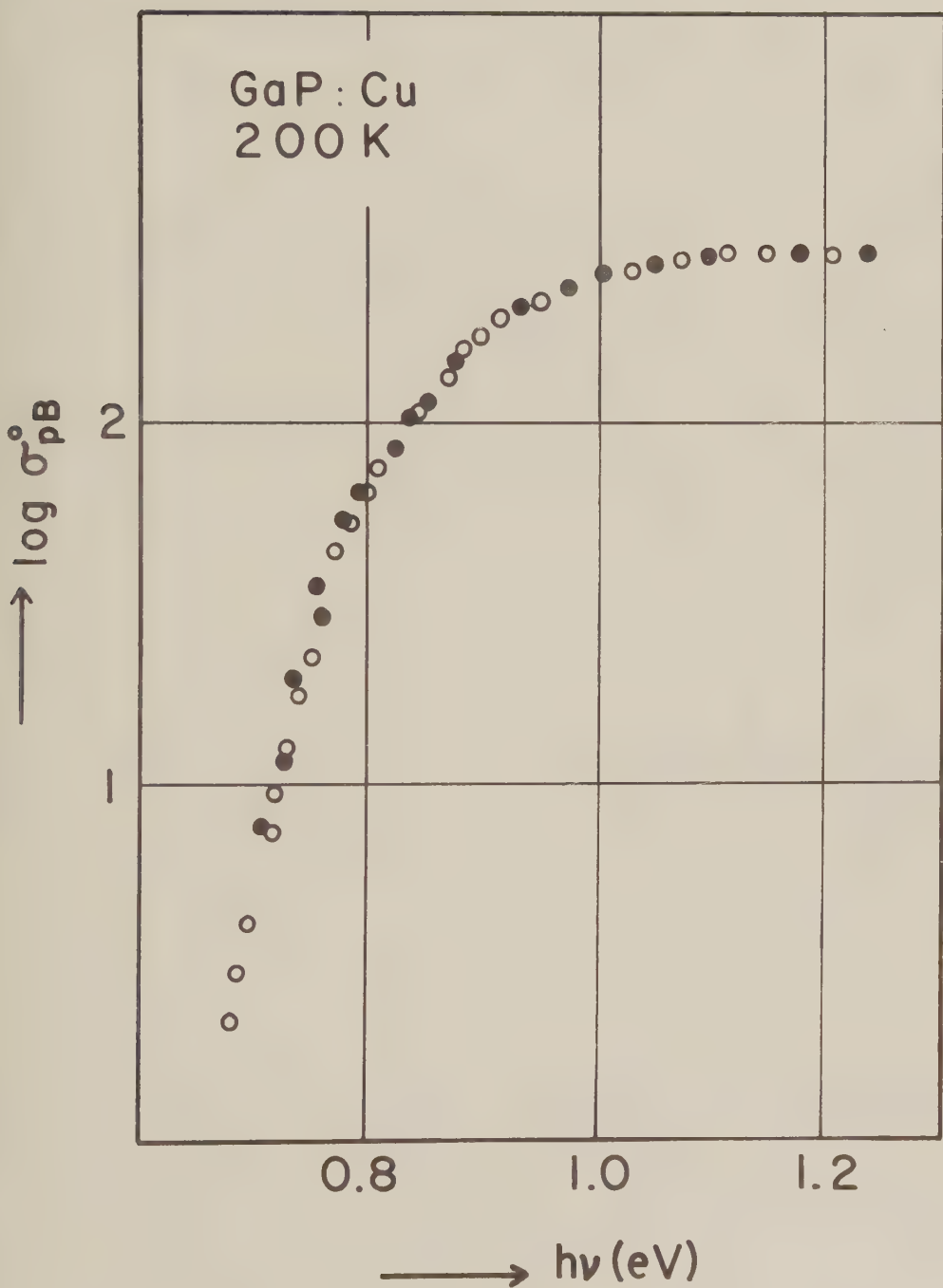
GaP: Cu
227

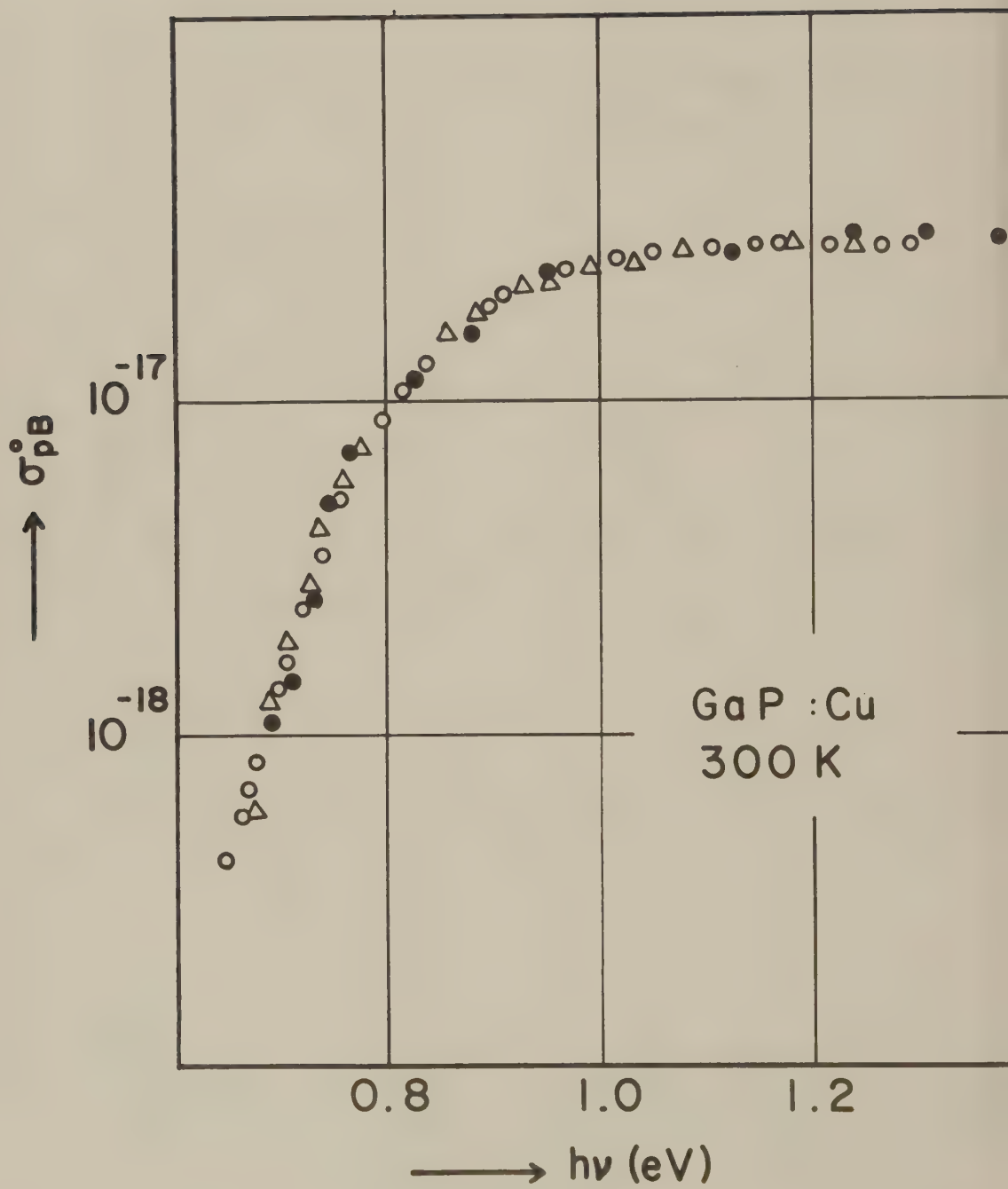
→ t (s)

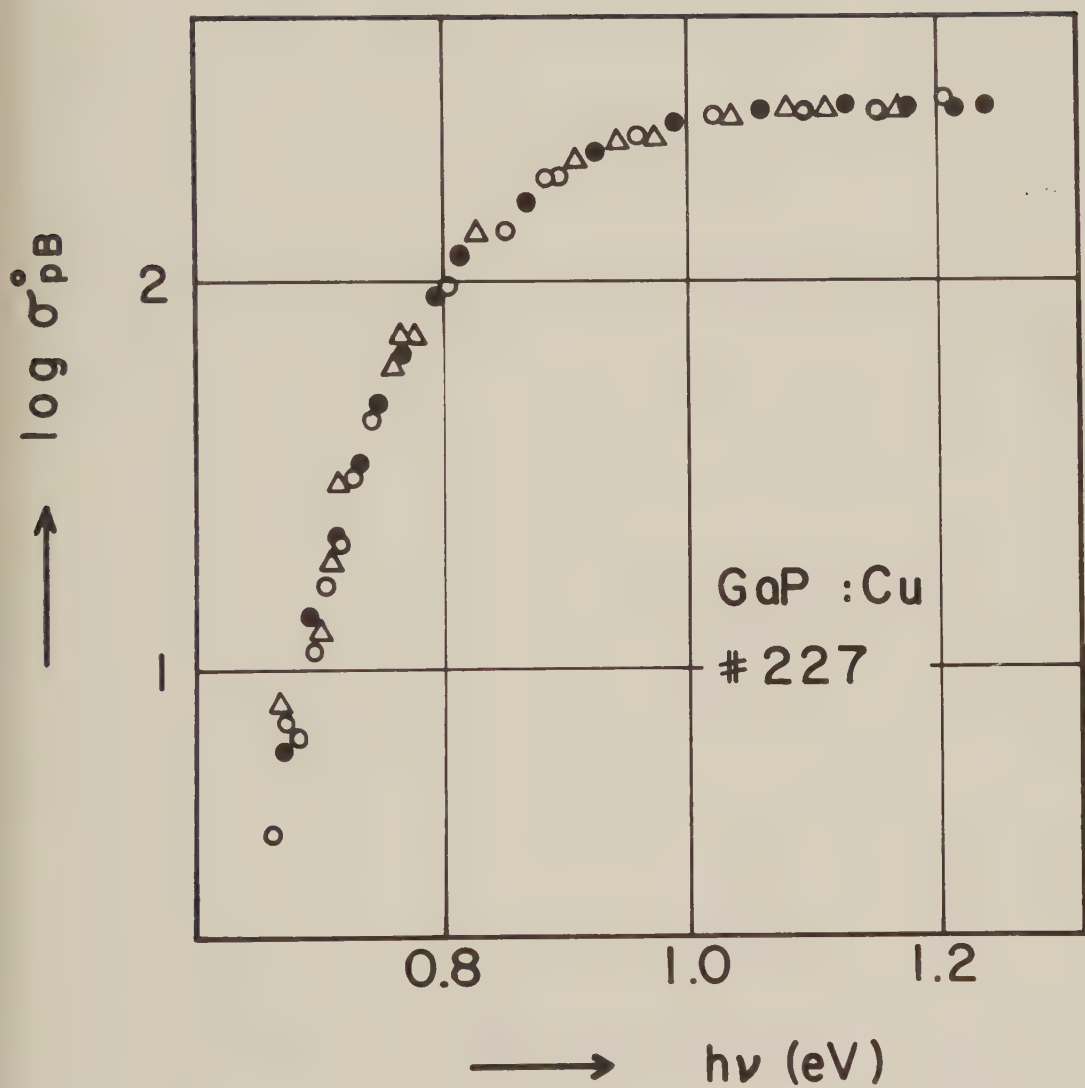


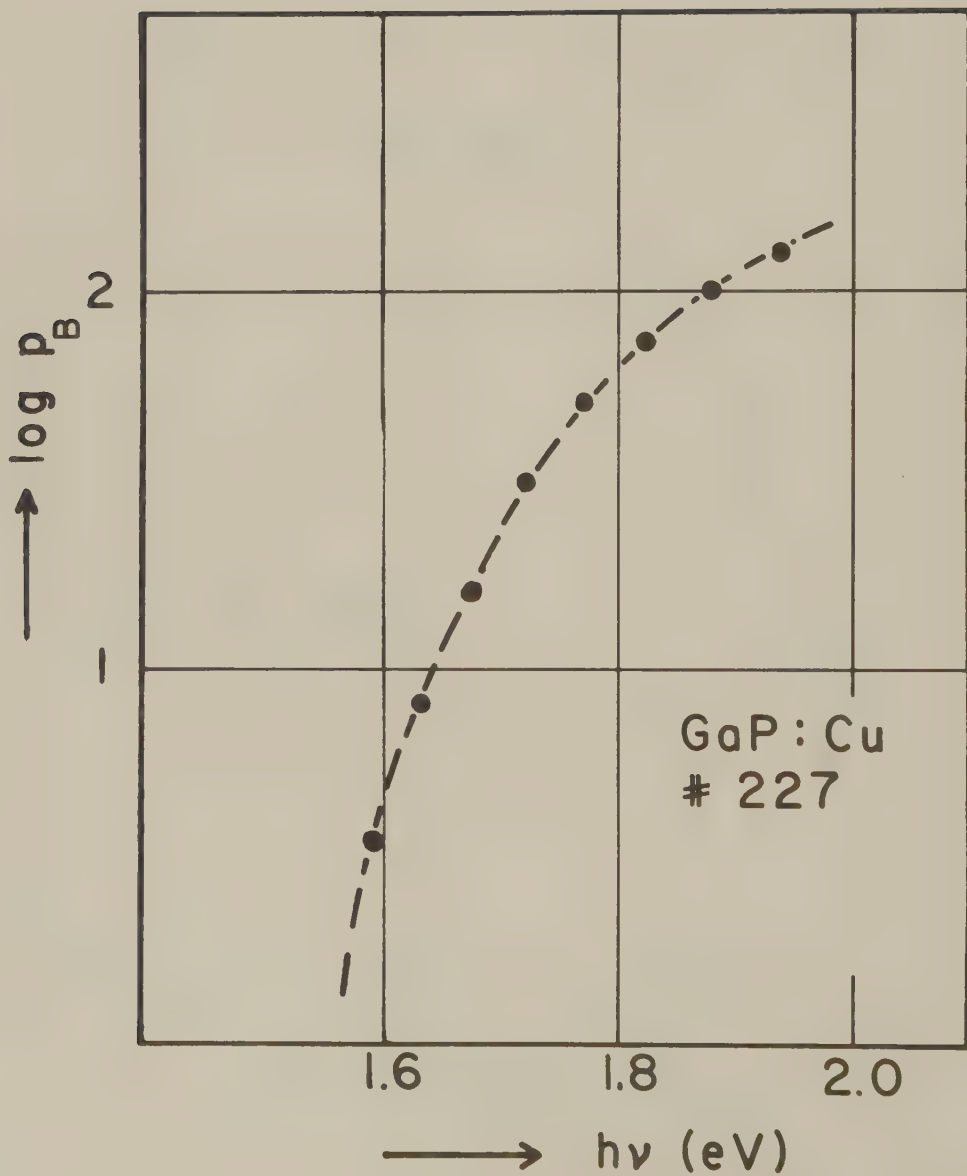


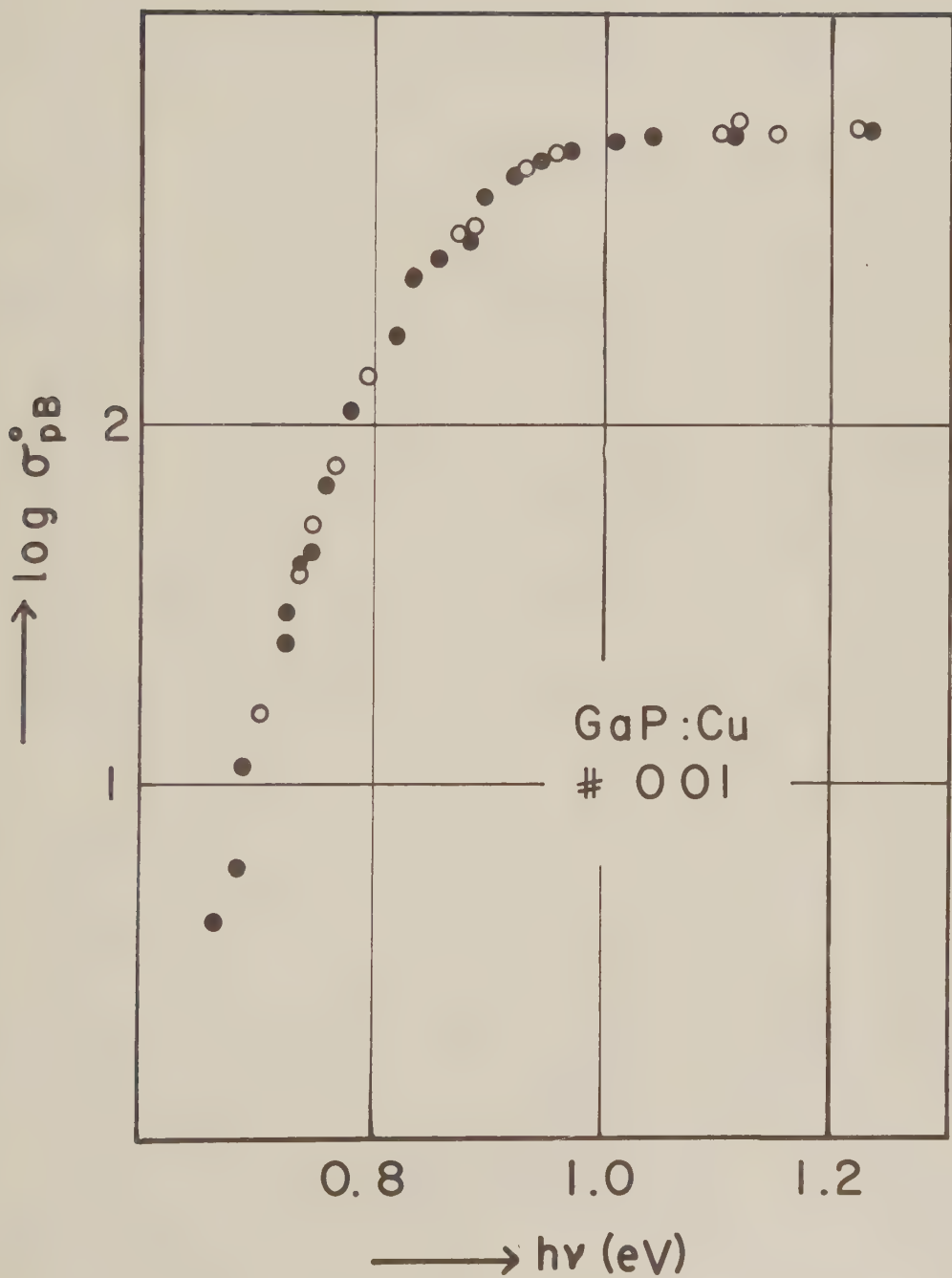


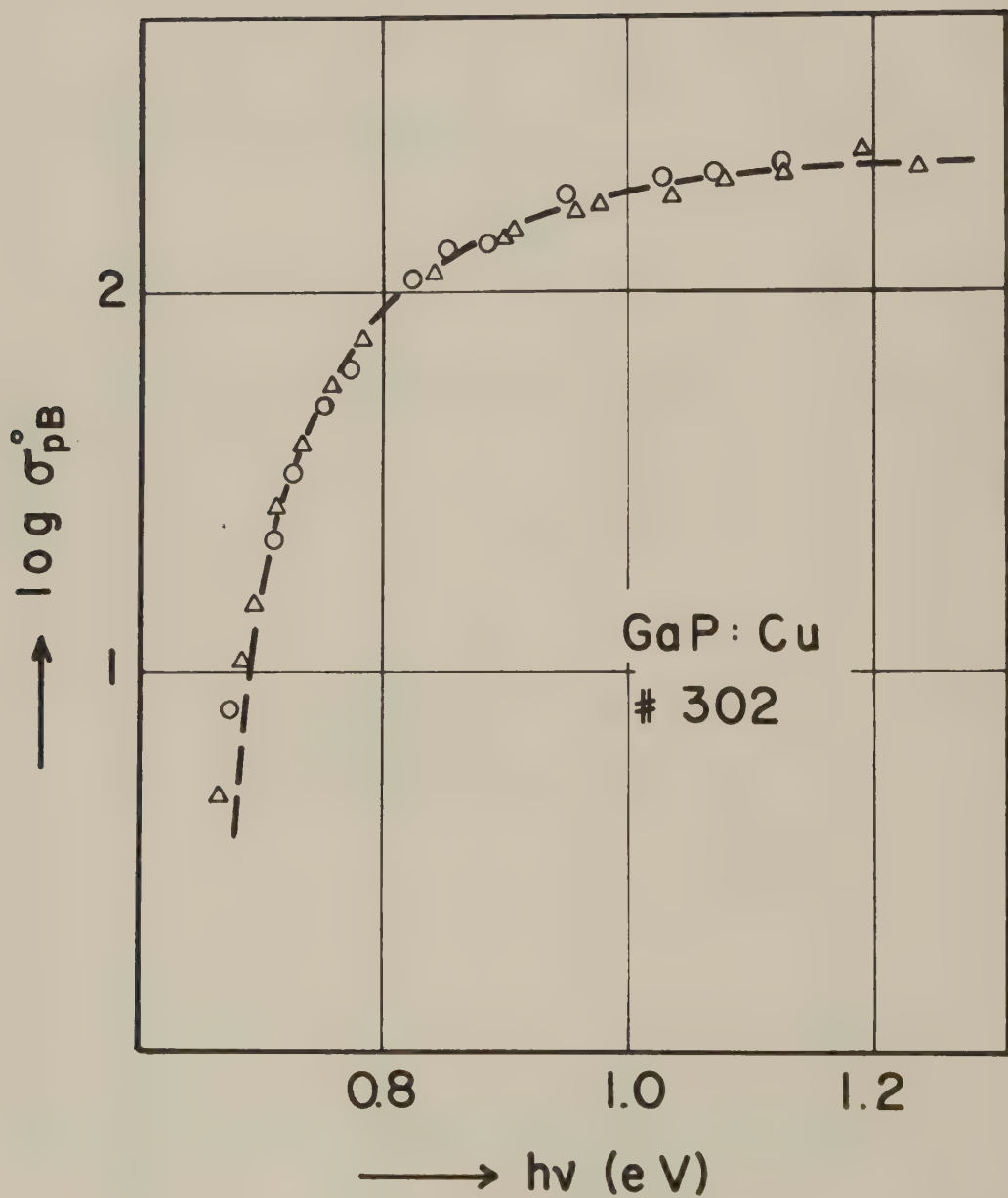


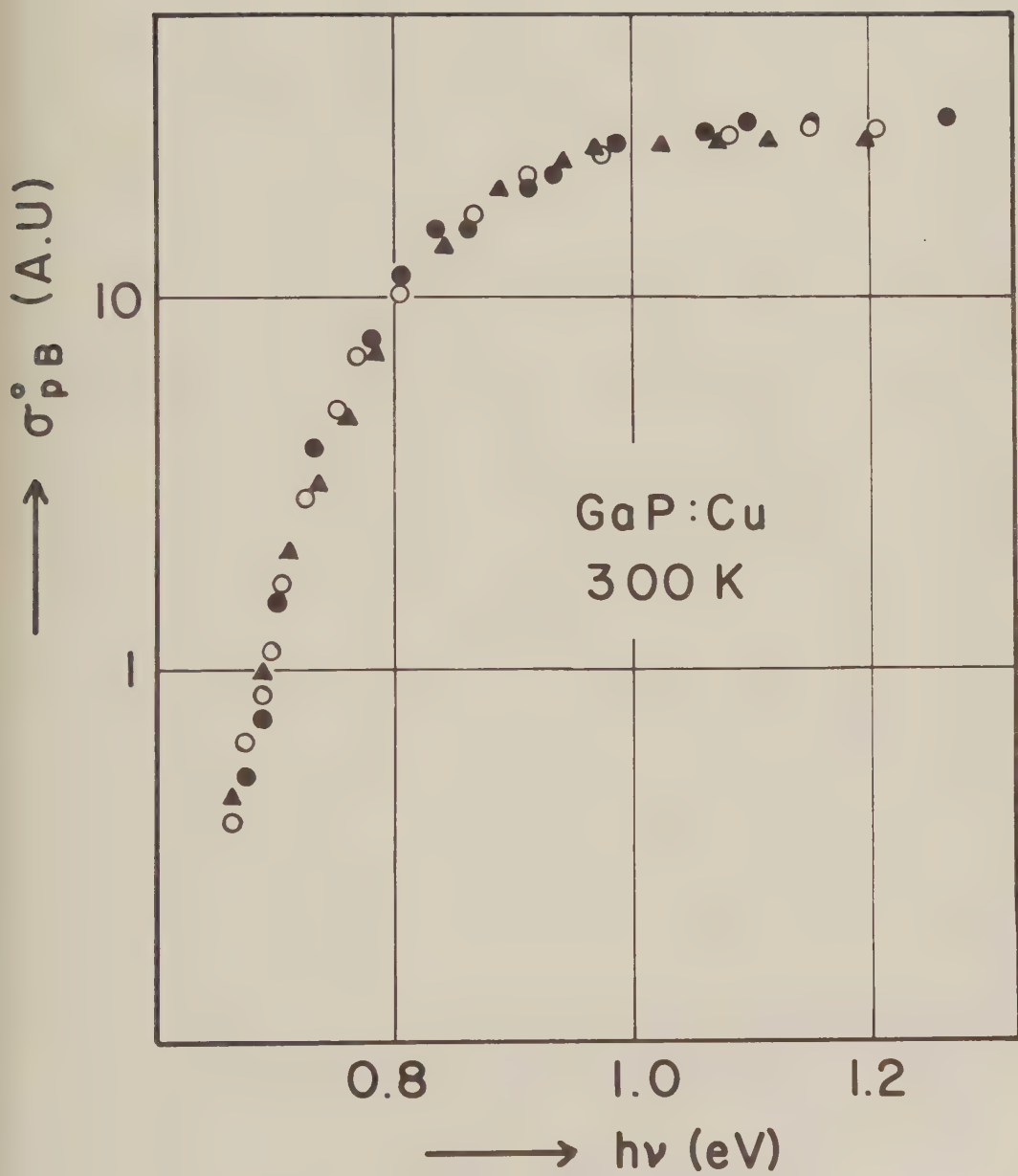


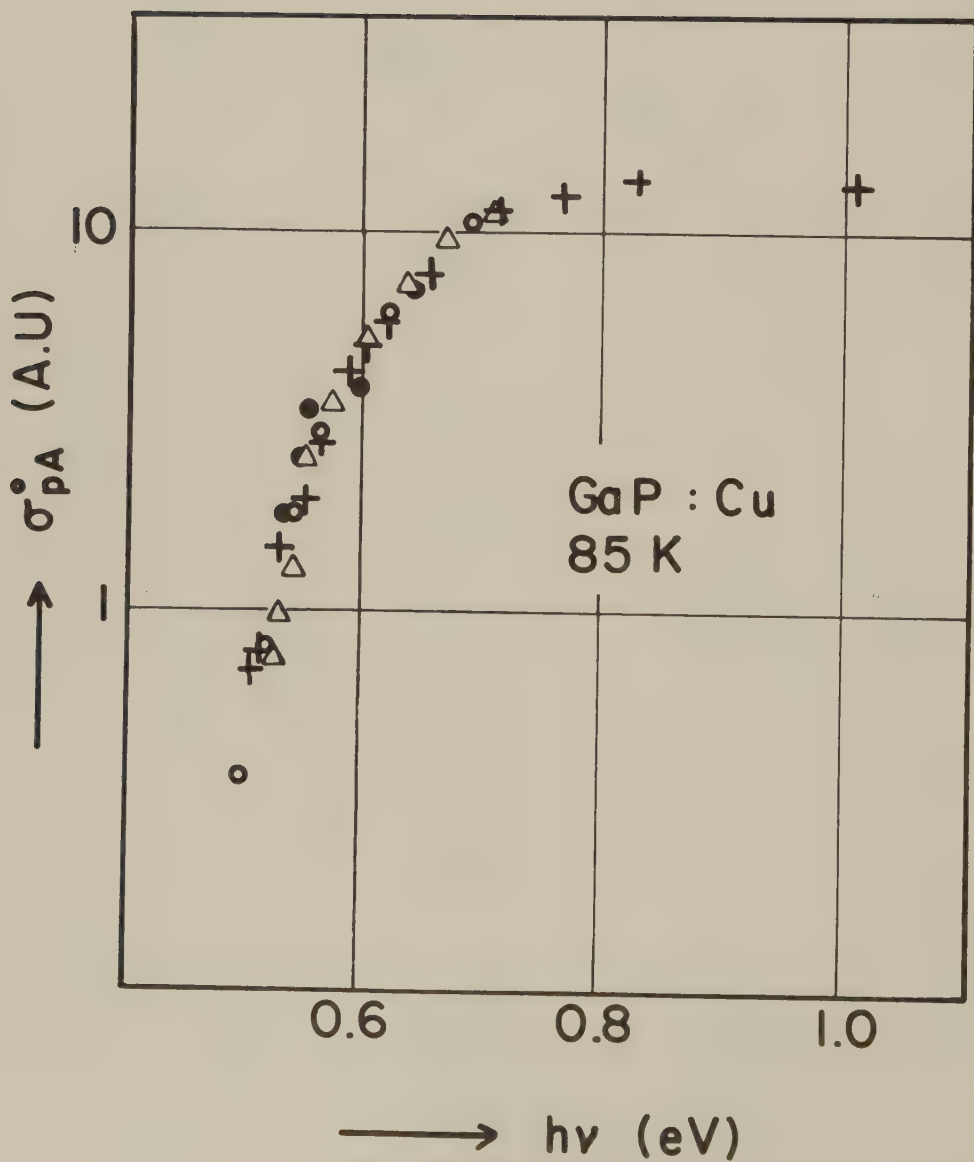


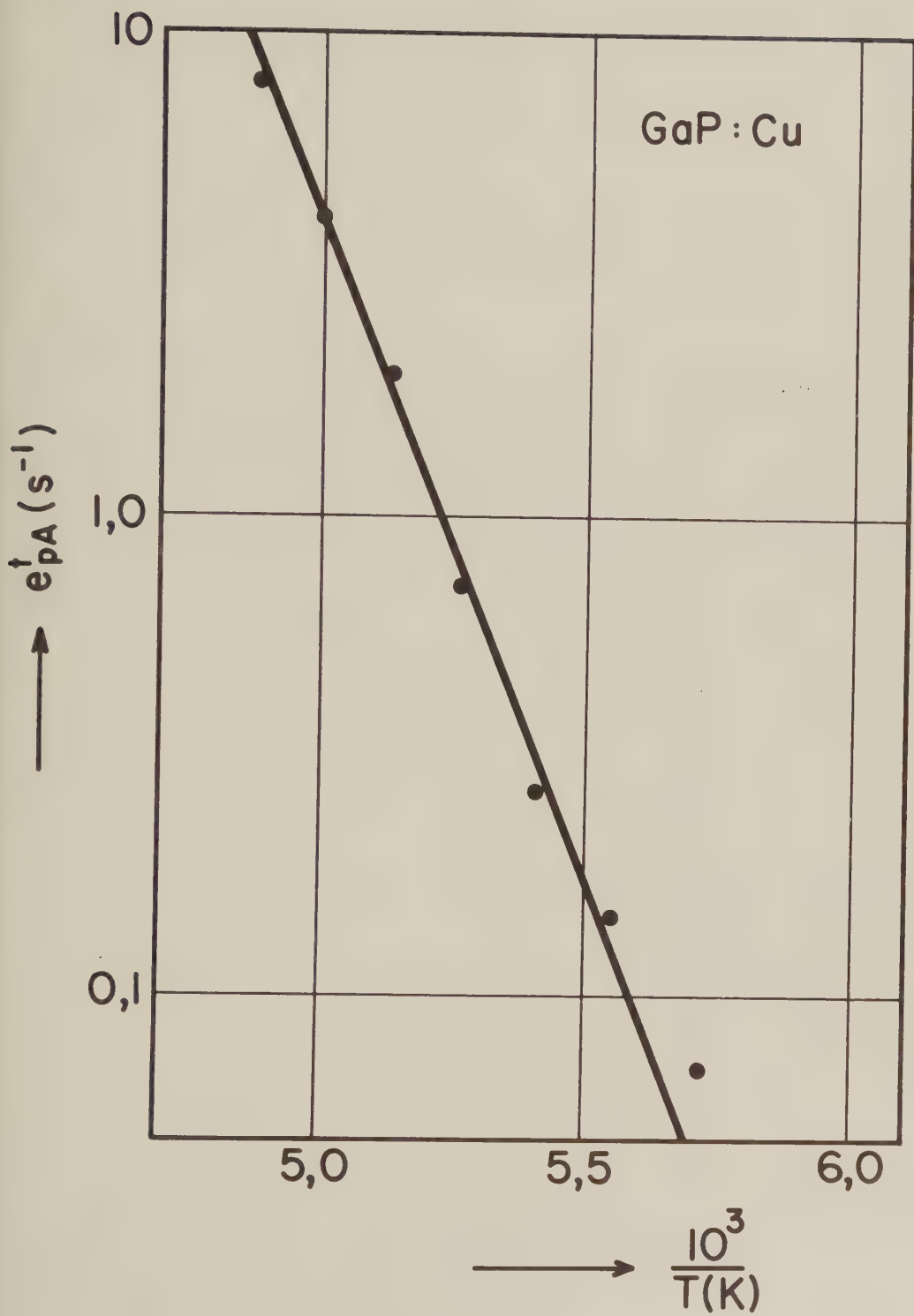


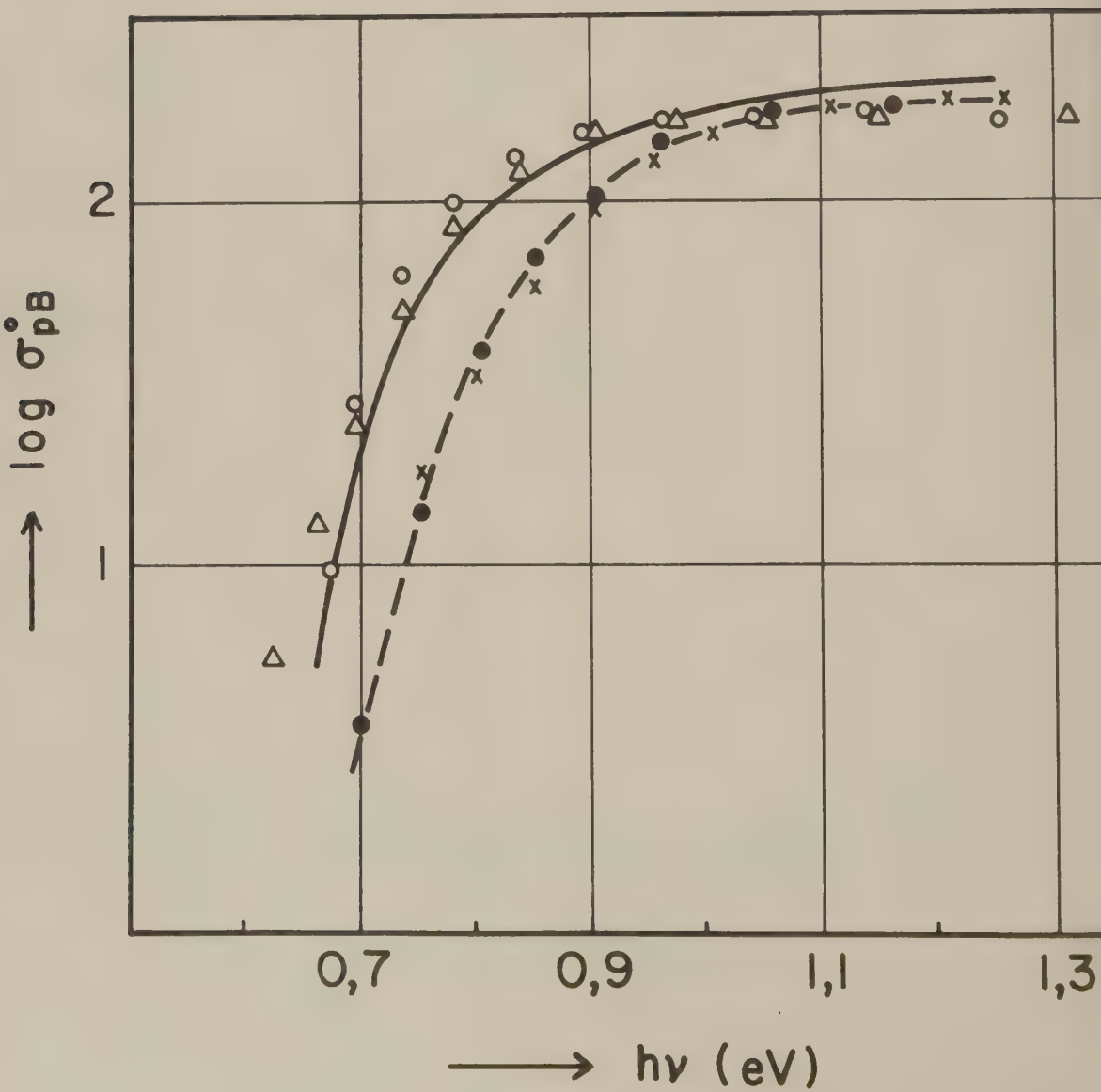












Capture and thermal emission rates for electrons and holes in Si:Pt.

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Introduction

During the last years there has been an intensive search for materials suitable for replacing Au as a lifetime-controlling element in Si devices, particularly in Si power devices. Pt has been extensively investigated in this connection ¹⁻¹⁵⁾. However, instead of an increased understanding of its properties, our knowledge of the Si:Pt system seems to become less certain and more confused as the number of investigations performed increases. This seems to be due to new investigation methods introduced during the last years ^{16, 17)}. However, we will show in this paper that most of the new levels reported do not result from better measuring techniques, but rather from limited understanding of the results obtained.

A detailed study of the optical properties of Pt-doped Si has earlier been reported from our department. These investigations have now been extended to measurements of the thermal emission - and capture-rates of electrons and holes. The results of all our measurements indicate that there are only two deep Pt-levels in Si.

Sample preparation

All samples were either p^+n or n^+p planar silicon diodes doped with platinum. The p^+n and n^+p diodes were diffused from 10 Ω cm n-type or p-type silicon slices

respectively and platinum was then diffused into them at about 900° C. Different methods of making ohmic contacts were tried, since especially measurements of capture cross-section are sensitive to bad contacts, i.e. contacts at which majority carriers cannot be either injected or extracted from the device without a substantial drop in voltage. To our experience well-preformed Ga, Al contacts work sufficiently well even at low temperatures. We had no problem getting good contacts to the highly-doped region, but could use ultra-sonic bonding of the top contact.

Experimental details

For our experiments, we have followed the generally-accepted techniques of measuring emission rates ¹⁸⁾ and capture cross sections ¹⁹⁾. That is, we have reverse-biased the diodes in dark and measured current- and / or capacitance-transients. We can then measure the rate of electron- (in p^+n -diodes) or holes- (in n^+p -diodes) emission for levels in the upper (p^+n) or lower (n^+p) half of the forbidden bandgap. Capture cross-sections have been measured by reducing the reverse-bias under short periods and then measuring the electron (p^+n) or hole (n^+p) occupancy as a function of the elapsed time without reverse-bias.

This approach is identical with that from Pals and our results are also in good agreement with his. By using light of energy of about 1eV we were able to fill both the donor- (to about 100%) and the acceptor- (to about 80%) levels with electrons. In a n^+p -diode we were therefore able to measure hole capture cross-section for both the acceptor and donor levels. This is the first time a "minority capture cross-section" has been measured directly in a neutral material and it therefore gives us an opportunity of comparing these values with other values of

minority capture cross-sections obtained in studies of minority carrier lifetimes, e.g. with these of Miller et al. The excellent agreement between our and these of Miller not only shows that these direct measurements are accurate, but also that the capture cross-sections are independent of the number of free holes, independent of whether these are minority carrier holes at about 10^{15} cm^{-3} .

Unfortunately, it was not possible in our sample to empty any of the donor levels in a p^+n diode because of the ratio for the optical cross-sections. We were therefore unable to measure the electron capture cross-section for the donor level.

To measure the capacitance transients, the Boonton 72 B C-meter was used and, the analog output from the C-meter being stored in a Nicolett 1090 transient recorder. To measure current transients a Keithley 427 current amplifier was used together with the Nicolett transient recorder.

To vary the temperature the sample investigated were placed in an Oxford CF 204 cryostate. The temperature were monitored using a Cu-constantan thermocouple with liquid nitrogen as the reference temperature.

The simple set up for measuring capture cross-sections shown in Fig 1 was developed. The risetime is limited to 5-10 ns by the fairly large capacitive loading of the 1/6 7404. This means that pulses shorter than about 50 ns should not be used. Since the RC constant of the diode is almost as large as the risetime, much shorter pulses would not be able to reach the pn-junction. Due to the transformer in the C-meter, it is essential to decouple the pulse from the C-meter to prevent the occurrence of "ringing". It is important to have a minimum

impedance from the Hi input to ground of at least 300 Ω , otherwise the C-meter will be inoperative. The pulse amplitude can be varied in the range 3-5 volts regardless of the dc bias.

Results

Thermal emission rates were determined from exponential decays. One such decay is shown in Fig 2. Emission data, plotted to allow for the T^2 dependence of $v_{th} \cdot N_{cv}$, are shown in Fig 3. Both the activation energies inferred from the fitted straight lines and the calculated cross-sections are presented in Table 1.

To measure the capture rate of electrons to the acceptor level a p^+n diode was used. The diode was reverse-biased at 85 K and subsequently illuminated by light of photon energy of 0.55 eV. This light will empty the acceptors and fill the donors with electrons. After removing the light the reverse-bias was reduced by 4V during 50 ns pulses. Using the same procedure with a n^+p diode the capture rate of holes to the donor was measured. Since it is possible to set the degree of occupancy of the acceptor level anywhere between 0 and 80 % by using extrinsic illumination¹²⁾ it was possible to measure even the hole capture of the acceptor. Fig 4 shows the capacitance decays obtained then holes are captured to the donor full circles and to both the acceptor and the donor open circles. The advantage of using 0.55 eV light instead of thermal emission is that we are able to choose the temperature independently and carry out all the measurements at constant temperature. The method is therefore superior to the original one, especially when one wants to measure the temperature dependence of the capture cross-sections. The capture cross-sections at 85 K are presented in Table 1. For comparison activation energies and capture cross-sections associated with platinum from the literature are also included.

ΔE_A eV ($E_C - E_T$)	σ_{RA}^{*} [10^{-15} cm^2]	σ_{RA} [10^{-15} cm^2]	σ_{PA} [10^{-15} cm^2]	ΔE_D eV ($E_T - E_V$)	σ_{PD}^{*} [10^{-15} cm^2]	σ_{PD} [10^{-15} cm^2]	σ_{ND} [10^{-15} cm^2]	REF
0.242	39			0.323	8.8			14
0.23		1.39		0.33		0.011		13
0.26			10	0.32			6	12
0.192	0.24			0.26	0.12			11
0.23		5		0.317		0.97		7
0.24		4.1	12.8	0.34		1.65	3.6	6
0.236	26	8.7	>11	0.293	1.3	0.66		This report

TABLE 1

Discussion

From our measurements of the thermal and optical properties of platinum doped silicon diodes and from the other information available in literature we conclude that platinum produces two main centers. One regarded as an acceptor, at about 0.23 eV below the conduction band and one regarded as a donor, about 0.31 eV above the valence band. Both centers are bound in n-type materials as well as in p-type materials. The concentrations of the centers are always equal, but the diffusion constant for Pt seems to be different in p- and n-type materials. If Pt is diffused into devices at very high temperatures (1100° C and above) for long periods of time, other centers cause by Pt-complex might be introduced. The technical importance of these latter centers are, however, open to question especially in power devices, since the obtained concentrations of these centers are very low at diffusion temperatures available. With our values of the cross sections, all values of measured timeconstants and diffusion lengths reported in the literature can be understood, leaving no need for any extra levels of uncertain origin.

Support from literature.

Our experimental results and our interpretation of the Si:Pt system are supported by the experimental results reported in all the six papers previously published, which contains both activation energies and capture cross-sections. This is true, even if some of the authors suggest quite different interpretations in their articles. We will therefore present a critical discussion of those six papers and challenge our model with their experimental results.

Pugnet et al: Like we, they report two levels with activation energies of $E_V + 0.323$ eV and $E_C - 0.242$ eV. From detailed balance, they obtain the value of $3.9 \cdot 10^{-14} \text{ cm}^2$ for the cross-section for electron capture of the acceptor ($E_C - 0.242$ eV). and $8.8 \cdot 10^{-15} \text{ cm}^2$ for hole capture of the donor ($E_V + 0.323$ eV). Due to the fact that the energy to be used in detailed-balance calculations is the binding energy at the temperature in question and not just an extrapolated activation energy, their values must be regarded as being close to those obtained in our measurements.

Evwaraye et al: From their DLTS measurements, they claim to have observed six different levels due to platinum doping. Our two platinum levels ($E_C - 0.23$ eV, $E_V + 0.33$ eV) are found as the main deep impurities. These centers are called the A- and E-centers. The center these authors claim to be the main recombination center, the B center ($E_C - 0.34$ eV), has not been observed by any other research group.

The reason for this is probably that this center is identical with the E center ($E_V + 0.33$ eV). It is also very likely that the D center is identical with the A center. The reason why they find the E center in a p^+n diode and the A center in a n^+p diode is that the junctions are not sufficiently abrupt or are not sufficiently asymmetric. The space-charge region will therefore extend also into the highly doped side. That is, both centers will show up in both measurements but, due to the doping profile, they will appear with quite different total capacitance changes. This interpretation is also supported from the fact that the presented curves for emission rates are almost the same for A and D and B and E respectively.

Knowing that both the A- and E-centers both are to be found in n- and p-type materials, one expects the so called B-center to disappear and to "invert" into a center in the lower half of the bandgap when the p^+n diode is pulsed in the forward direction. This effect can be seen in their Fig 4 and explains why they do not observe the B-center in their injection experiments. The conclusion is that the A and the D centers are the same centers and that the B and the E and probably the F centers are one and the same center. The remaining center, the C-center, has never been attributed to platinum by any other author, but might perhaps be a platinum complex or a surface state. We leave it to the authors to give an erratum on the calculations presented in Table III.

Miller et al: They find only two centers due to platinum diffusion. The agreement between their values of capture cross section and activation energies and ours are reasonable. Even in their TSC-measurements the effect of not having perfect p^+n or n^+p diodes is seen. I.e., both levels turn up in both n^+p and p^+n diodes, just as they did for Ewvaraye et al. However, Miller et al make a correct interpretation and do therefore report only two rather than four Pt-levels.

Lisiak et al: From a complex formula, they deduce two different centers in p-type as well as in n-type materials, in all four centers. The reason why they need the complex formula is that they obtain a substantial degree of compensation from platinum diffusion. Though they use a complicated formula, they do not take into account the recombination which occurs in the ends of the space-charge region due to the carrier "tails" into the space-charge region which will give a different time constant

for this region. If the material is heavily compensated by the deep impurities, the parameters in the "exact" formula used by Lisiak et al will depend critically on the exact doping profile and the parameters can even change during the transient. If the diode for example is not perfectly asymmetric and abrupt even the geometrical point of the pn-junction will shift during the measurement. This makes it very unreliable to use highly compensated materials, even if "exact" formulae are used. The interesting fact that only the centers with low concentrations can be measured with the current-transient and admittance-spectroscopy methods is not commented on. To quote Lisiak et al "The E_{III} level shown is of uncertain origin." Since the properties of this level disagree with those of all other levels found, we will not commentate on this level. The E_{IIA} and E_{ID} might be one level but, because the authors try to fit the non-perfect decay to their formula, the decay may split into two branches, one fast, the other slow. The measurements above the crossing agree within experimental errors with ours and those of Evwaraye et al. Based on incorrect values of capture cross-sections Lisiak et al claims the E_{IIA} level to be the main recombination center. Using SEM, they obtain a high injection time constant of 4.5 ns for Si diffused with Pt at 1000°C. If we calculate the expected time constant from $\tau = \tau_{no} + \tau_{po}$ and use the Pt_I concentration of $8 \cdot 10^{15} \text{ cm}^{-3}$ from Lisiak et al and our value for the acceptor level, we obtain $\tau_{no} = 1.4 \text{ ns}$, $\tau_{po} = 1.1 \text{ ns}$ and $\tau = 2.5 \text{ ns}$. This agreement is good enough to indicate that the acceptor level and not any Pt_{II} -level is the level controlling the life time.

Pals: He carried out measurements similar to ours and obtained results close to ours. He does not claim that there is only two levels caused by platinum, since he doubted if he could detect the presence of an acceptor in the

lower half of the bandgap, the level at $E_v + 0.36$ eV claimed by Carchano et al. The situation is in fact the converse, he should have seen such a level if it was present, but he could not determine from his measurement if the center is an acceptor or a donor. The conclusion is that also in his sample there are no more than two levels caused by platinum.

Conti et al: Already in 1971 they found two levels caused by platinum, one at $E_c - 0.24$ eV, the other at $E_v + 0.34$. In view of the details of their experiment, the higher temperature and diode recovery time-constant measurements, their results are in agreement with our.

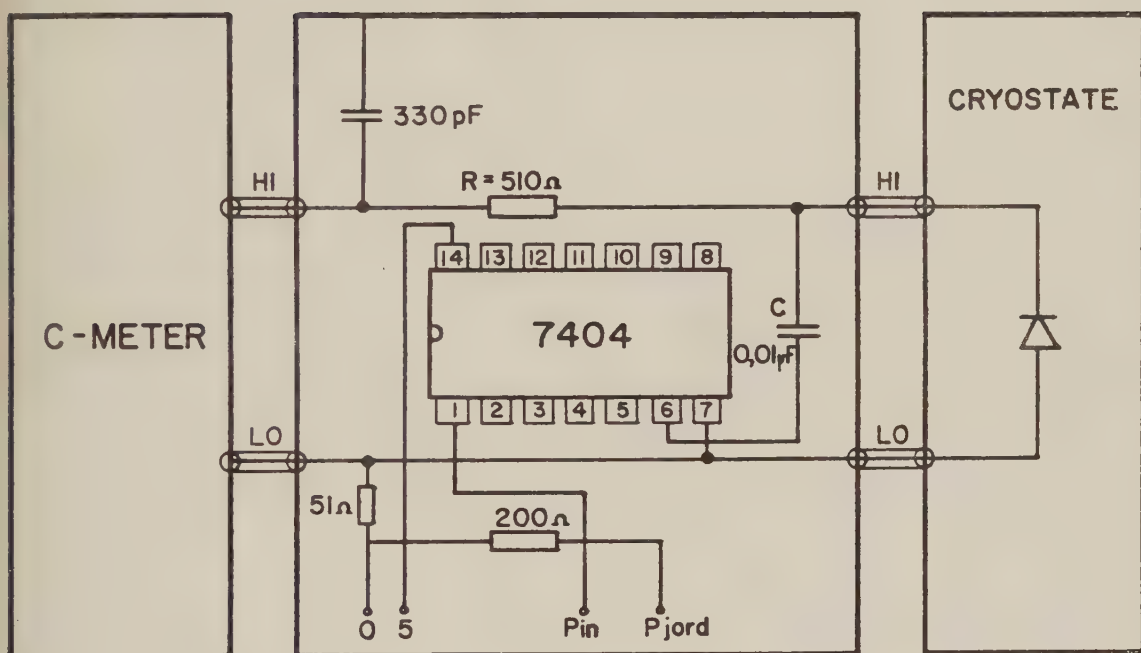
From all this, we conclude that the technically important issue of Pt-doping is clarified, namely that Pt introduces two levels. One level situated 0.23 eV below the conduction band. The electron capture cross-section to this level is $9 \cdot 10^{-15} \text{ cm}^2$ and the hole capture-cross section $\geq 11 \cdot 10^{-15} \text{ cm}^2$. The other level is 0.3 eV above the valence band and the capture cross-section for holes is $0.7 \cdot 10^{-15} \text{ cm}^2$.

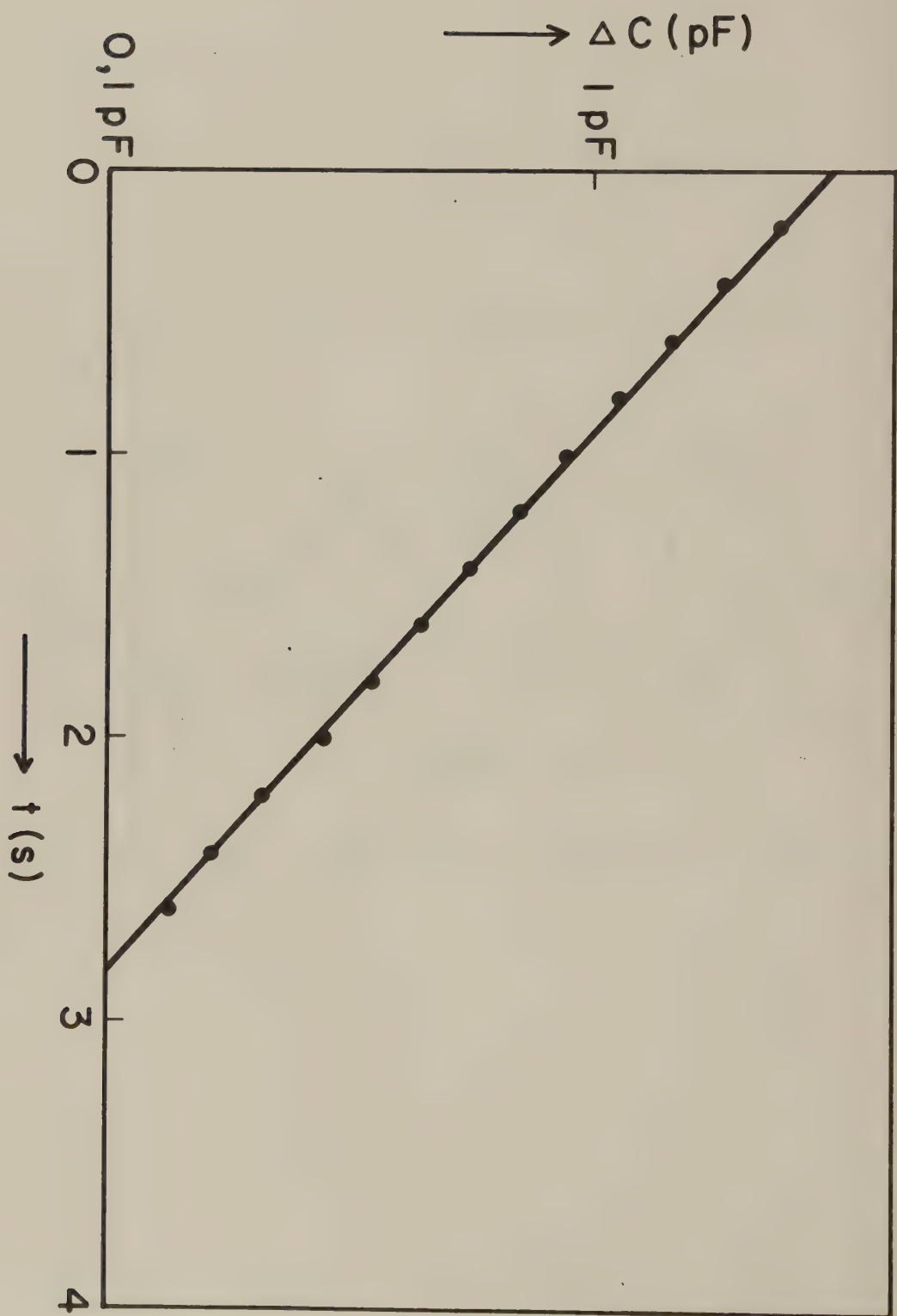
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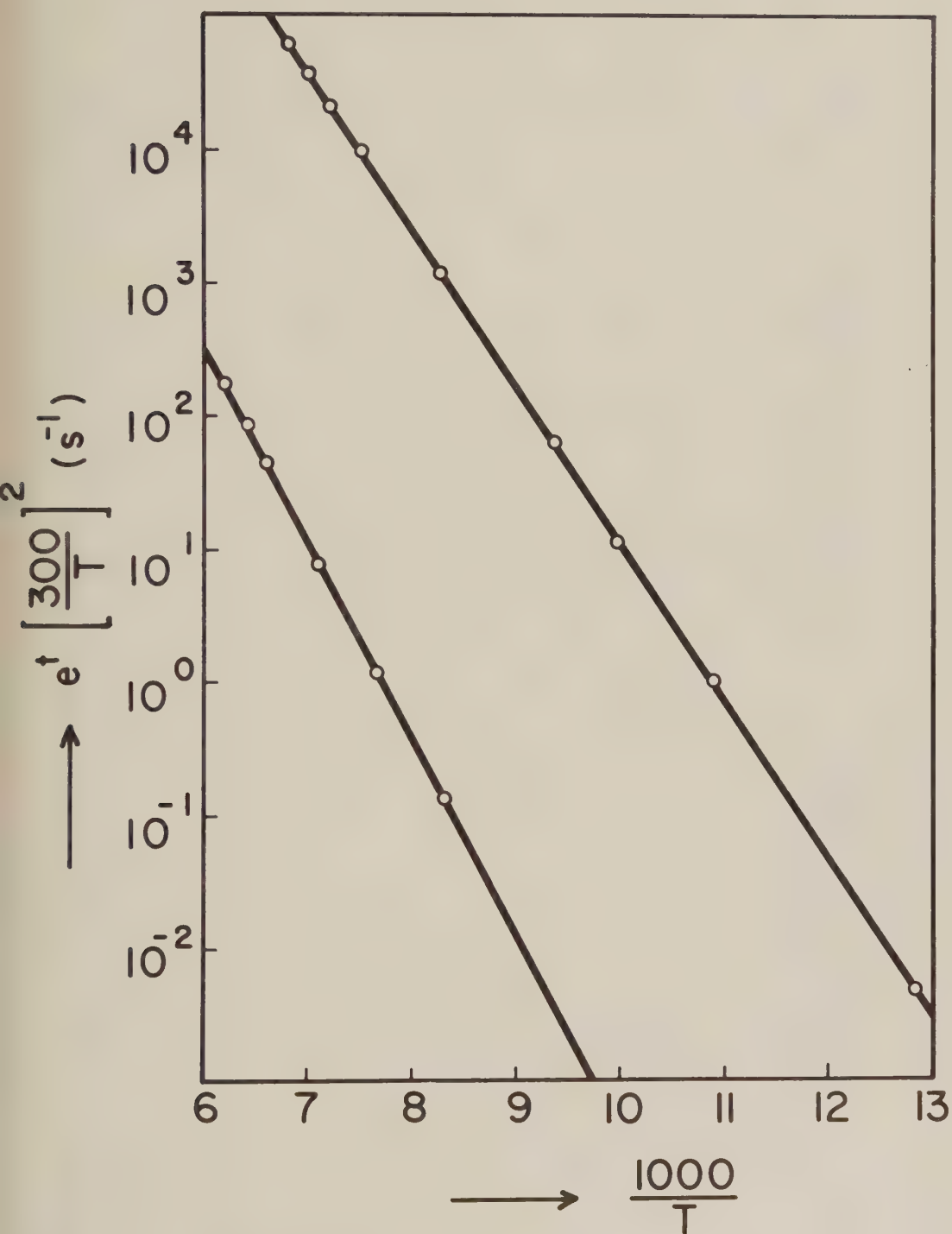
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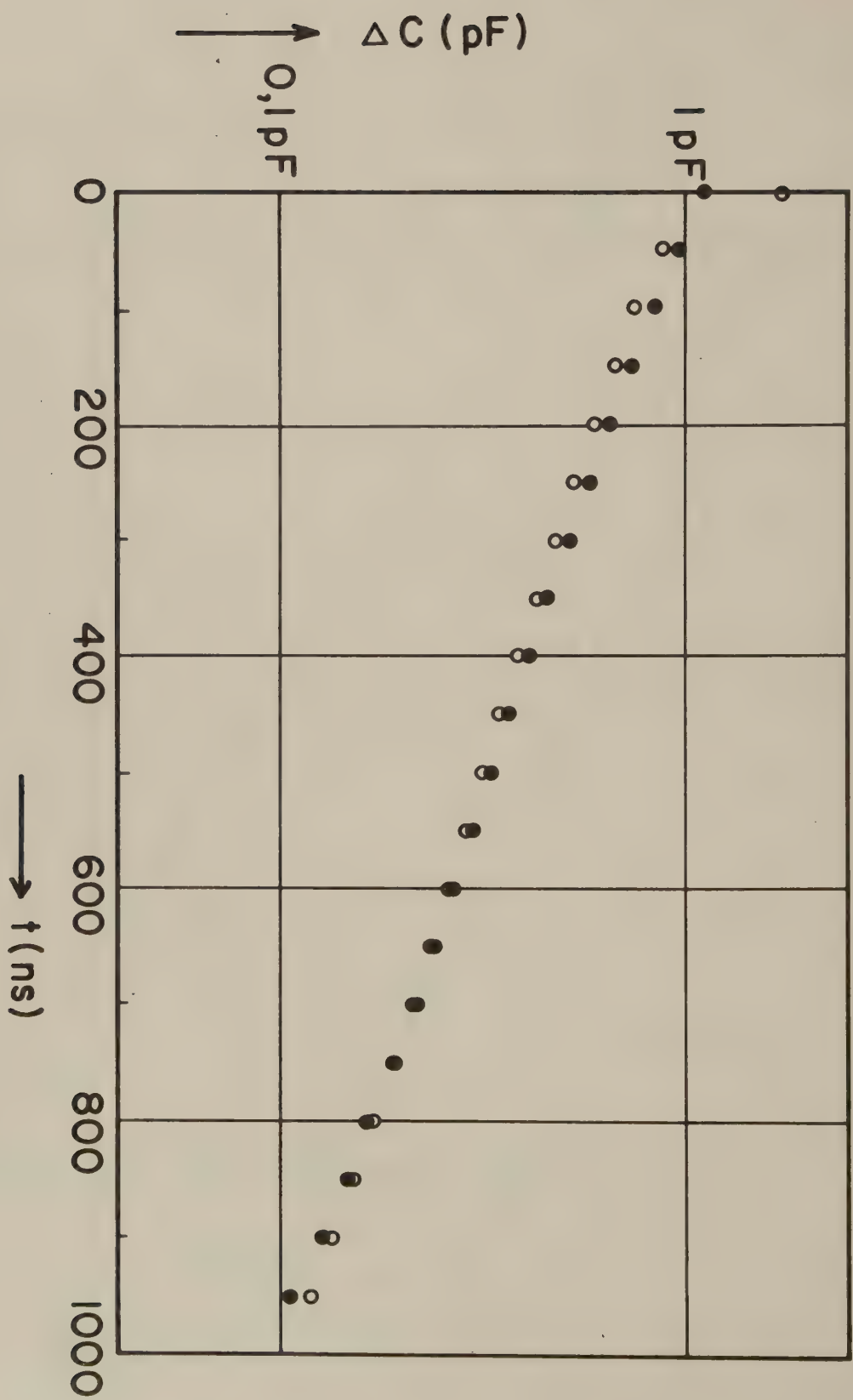
Figure captions

- Fig.1 The set-up for measurements of capture cross-sections. The pins 2-13, 3-12, 4-11, 5-10, 13-9 are connected. Usable ranges of the Boonton 72 C-meter: 10 pF and above.
- Fig.2 C-transient due to thermal emission of electrons from the acceptorlevel ($E_c - 0.23$ eV) at 100 K.
- Fig.3 The emission rates, corrected for T^2 dependence of $N_{v,c} v^t$, versus invers temperature. Full circles emission of electrons to the conduction band, open circles emission of holes to the valence band.
- Fig.4 C-decay after pulses of 50 ns due to capture of holes to the donor (full circles) and to both the donor and the acceptor (open circles).









TSC measurements and their correlation with photocurrent techniques.

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Deep level energy spectroscopy using thermal release of trapped charge in pn junctions or Schottky barriers has recently been suggested as a useful method for evaluating deep level parameters in semiconductors ^{1) 2)}. Although the measurements of thermally stimulated currents (TSC) may be a rapid method the use of which simplifies the initial characterization of known deep centers in unknown samples, considerable difficulties arise when TSC measurements are used for the characterization of unknown deep levels.

In this letter, we describe the investigation of a deep level in copper doped GaP p^+n junctions using the TSC method. A comparison is made between results obtained using the TSC method and those obtained from the photocurrent technique and the reliability of the TSC data is discussed. Furthermore, an extension of the TSC method to minority carrier traps by combining thermally stimulated processes with optical excitation processes is presented.

The diode used has previously been investigated by photocapacitance and photocurrent techniques and detailed information concerning the properties of the deep impurity level was available ³⁾. The particular deep center investigated here, the A-center, has a level 0.5 eV above the valence band and a thermal capture cross section for holes σ_{pA}^t of about $2 \cdot 10^{13} \text{ cm}^2$ at 170 K ³⁾. From optical quenching of photoluminescence, it may be assumed that the optical threshold energy for holes ΔE_{pA}^0 is temperature dependent ⁴⁾. GaP p-n junctions containing copper impurities have been investigated by Fabre and Bhargava ²⁾ using thermally stimulated current measurements. In n^+p diodes, the TSC spectrum showed four distinct peaks at about 129 K, 175 K, 239 K and 320 K. The energy levels of these traps have been determined as 0.22 ± 0.02 , 0.29 ± 0.02 , 0.39 ± 0.03 and 0.55 ± 0.03 eV respectively. The constant heating rate was $\approx 0.5^\circ \text{ K s}^{-1}$. The deep level at 0.55 eV has been interpreted as the ionization energy of an acceptor level related to copper. Because the value of 0.55 ± 0.03 eV is very close to the thermal activation energy of the A-center in our copper doped GaP samples ³⁾, this lends support to the idea that the 0.55 eV level could be the A-center.

The results presented in this paper have been obtained with a copper doped GaP p^+n diode. The sample was forward biased and cooled down to 77 K in darkness in order to find out whether there are deep centers in the upper part of the bandgap. With 4 V reverse bias applied, it was then heated up to about 250 K, the heating rate being 0.33 K s^{-1} . The TSC spectrum showed two small peaks, the temperatures of the emission profile maxima occurring at 126 K and 155 K. (Fig 1a, dotted curve). Next, the sample was again cooled down to 77 K in darkness and illuminated with light

of photon energy 1.91 eV to recharge centers in the lower part of the bandgap. Because we were interested only in the A-center, the sample was also illuminated with light of photon energy 0.46 eV before being heated up with the 4 V reverse bias applied. Two distinct peaks, one at 171 K and a smaller one at 131 K were observed (Fig 1a, dashed curve). Neither of them was detected in the first run and it can therefore be concluded that they are due to levels in the lower part of the bandgap. To make certain that the distinct peak at 171 K is correlated with the A-center, the sample has also been illuminated with light of photon energy 0.59 eV after being cooled down in darkness and illuminating it with 1.91 eV light. Heating up the sample with a reverse bias of 4 V applied, the TSC spectrum showed only one very small peak at 137 K (Fig 1a, solid curve). This proves that the activation energies of the centers, yielding the two peaks in the TSC spectrum at 131 K and 171 K, are in the range between 0.46 and 0.59 eV, contradicting the results of Fabre and Bhargava ²⁾. A more accurate determination of the thermal activation energy was therefore performed by measuring the shift of the 171 K peak in the TSC spectral response with the heating rate β ^{1) 2)}. Plotting the logarithm of T_p^2/β versus $1/T_p$, a thermal activation energy of 0.57 ± 0.04 eV is found. It should be noted that a value of about 0.57 eV corresponds to the linearly extrapolated absolute zero-energy ΔE_{po}^t ⁶⁾ and is therefore in fair agreement with the optical activation energy of the A-center $\Delta E_{pA}^0 = 0.5$ eV as determined from photocurrent measurements ³⁾.

Assuming a temperature independent attempt to escape frequency

$v = \sigma_p^t v N_V g^{-1}$, the following relation ¹⁾ can be used to calculate the thermal capture cross section for holes σ_p^t :

$$\frac{vkT_p^2}{\beta \Delta E_{pA}^t} = \exp (\Delta E_{pA}^t / kT_p)$$

Here ΔE_{pA}^t is the thermal activation energy at the temperature of the emission profile maximum, v is the thermal velocity of holes, N_V is the valence band density of states and g is a degeneracy factor. Taking $T_p = 171$ K, $g = 1$, $v = 9.06 \cdot 10^6$ cm s⁻¹, $\beta = 0.33$ K s⁻¹ and instead of ΔE_{pA}^t the more accurate value $\Delta E_p^0 = 0.5$ eV from optical measurements and neglecting any Franck Condon shift, a value of $5.1 \cdot 10^{-13}$ cm² is calculated for σ_{pA}^t . This value is in good agreement with results obtained previously ³⁾ and confirms the correlation of the peak at $T_p = 171$ K with the A-center in GaP:Cu.

The most serious drawback of TSC measurements is the difficulty of correlating the measured temperature with the actual temperature of the specimen. Although the temperature of the pn-junction has been determined from the temperature dependence of the dark current at constant forward bias measured under steady state conditions, the reproducibility was not better than ± 0.25 K. If the reproducibility is ± 0.5 K, this implies for the investigation reported here an error in the thermal activation energy, determined from the shift in the TSC spectrum with β , of the order of ± 0.06 eV. In many cases, this error is much too large to permit an unambiguous identification of deep centers. However, if the activation energy of the center to be investigated is

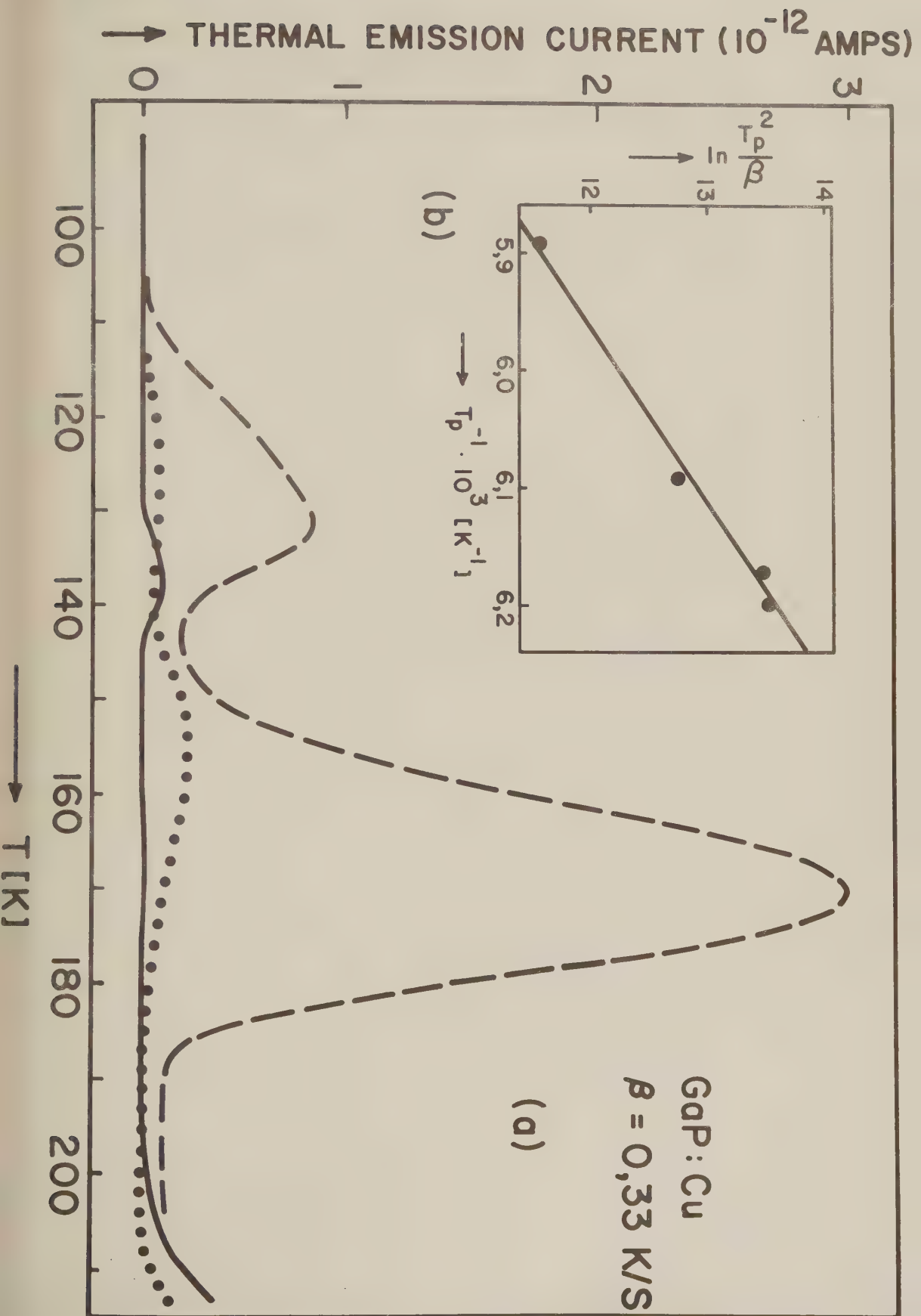
known from other measurements, TSC measurements provide a useful method for a rapid characterization of semiconducting materials.

If the thermal activation energy of 0.57 eV as determined from our TSC measurements had been used for calculating σ_{pA}^t instead of the more accurate ΔE_{pA}^0 value, a value for the capture cross section is obtained which differs by more than two orders of magnitude from that obtained from thermal emission rates ³⁾. On the other hand, if the data of Fabre and Bhargava are used ²⁾, a capture cross section of about $4 \cdot 10^{-20} \text{ cm}^2$ is found for all acceptor states in GaP investigated by these authors. This value is more than four orders of magnitude smaller than those published by Smith ¹⁾ and more than seven orders of magnitude smaller than the value for σ_{pA}^t presented in this paper. Large capture cross sections are not unusual in GaP. For example, Smith ¹⁾ measured a capture cross section of $1.4 \cdot 10^{-14} \text{ cm}^2$ for a majority carrier trap in n-type GaP using the TSC method and Lang and Henry ⁷⁾ found a value of about $2 \cdot 10^{-14} \text{ cm}^2$ for oxygen (state 2) in GaP.

In conclusion, we have shown that TSC measurements can be used for the investigation of both majority carrier and minority carrier traps. Although the TSC technique provides a useful method for monitoring known centers in different samples, difficulties often arise for an unambiguous evaluation of the parameters of deep levels.

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An alternative method of measuring photoionization cross -
sections in photoconductors

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Abstract

A new method of measuring photoionization cross sections in homogenous material is described and discussed. Its main idea is to keep the occupancy of deep levels almost constant with a high intensity constant light source and to measure small changes in current caused by a second alternating light source using a sensitive lock-in-amplifier method.

An alternative method of measuring photoionization cross sections in photoconductors

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1. Introduction

New measuring techniques have been developed in recent years for investigating the physical properties of deep level impurity centers in semiconductors. Most of these techniques make use of excitation processes via deep impurity levels in the space-charge region of a p-n junction or metal-semiconductor barrier¹⁻³⁾. Although important parameters such as optical and thermal emission- and capture-rates are easily obtained from these measurements, nevertheless, these methods have certain drawbacks. For example, low leakage current is required for devices measured by photocurrent techniques. Photocapacitance measurement is a differential method and is therefore limited by the resolution of the capacity meter or bridge⁴⁾. Furthermore, these measurements involve fields of the order of $10^4 - 10^5$ V/cm. Some of these drawbacks can be avoided by using data from photoconductivity measurements. The electric field in a photoconductor is,

for example, usually smaller than 10^2 V/cm and can therefore be neglected in many contexts. In addition, the need for pn-junctions or Schottky barriers with low noise and a minimum of leakage current is not required. However, the measurements may be vitiated by long decay times which in certain cases can amount to hours ⁵⁾. The photocurrent technique then not only becomes rather unreliable, but also makes the measurements lengthy. Furthermore, in most materials the photo-conductivity current is a complex function of optical emission and capture rates and information of about these parameters cannot therefore be obtained by a straightforward analysis. This is easily seen by considering a single deep energy level of concentration N_T in the upper half of the bandgap at energy E_T in an n-type semiconductor. For photon energies $h\nu < E_T - E_V$, where E_V is the top of the valence band, the free electron concentration n in the conduction band is given by ⁵⁾.

$$n = -\frac{e_n^0}{2c_n} + \sqrt{\left(\frac{e_n^0}{2c_n}\right)^2 + N_T \frac{e_n^0}{c_n}} \quad (1)$$

for high excitation densities and

$$n = \sqrt{N_T \frac{e_n^0}{c_n}} = \sqrt{N_T \frac{\sigma_n^0}{c_n}} I \quad (2)$$

for small excitation densities, when recombination is taken into account.

$e_n^0 = \sigma_n^0 \cdot I$ is the optical emission rate of electrons and c_n is the sum of the optical and thermal capture rates. The material often contains more than one energy level and the simple form of eq2 then changes to $n \sim (e_n^0)^f$ where $0 < f < \infty$. Since f might vary with photon energy, photon flux and/or temperature corrections are difficult to make in many cases.

The purpose of this paper is therefore to present a sensitive method by which photo-conductivity measurements can be used to determine the photo-ionization cross-sections of deep impurity levels as a function of photon energy. To demonstrate how the spectral distributions of photo-ionization cross-sections of deep level impurities are determined from such photoconductivity measurements, we consider a shallow energy level of energy E_s and a deep energy level of energy E_T , both in the upper half of the bandgap in an n-type material. Using a light source with intensity I_0 and photon energy $h\nu_0$, the differential equations describing the system are

$$\frac{dn_T}{dt} = -\sigma_1^0 (h\nu_0) \cdot I_0 \cdot n_T + \frac{n}{\tau_{pT}} \quad (4)$$

$$\frac{dn_s}{dt} = -\sigma_2^0 (h\nu_0) \cdot I_0 \cdot n_s + \frac{n}{\tau_{ps}} - e_{ns}^t \cdot n_s \quad (5)$$

$$\frac{dn}{dt} = \sigma_1^0(h\nu) \cdot I_0 \cdot n_T + \sigma_2^0(h\nu_0) \cdot I_0 \cdot n_S - \frac{n}{\tau} + e_{ns}^t \cdot n_S \quad (6)$$

The temperature has been adjusted so that thermal excitation processes from the deep impurity level can be neglected.

Using a second light source with intensity I_1 and photon energy $h\nu_1$, eq 6 will be transformed to

$$\begin{aligned} \frac{dn}{dt} = & \sigma_1^0(h\nu_0) \cdot I_0 \cdot n_t + \sigma_1^0(h\nu_1) \cdot I_1 \cdot n_T + \sigma_2^0(h\nu_0) \cdot I_0 \cdot n_S + \\ & + \sigma_2^0(h\nu_1) \cdot I_1 \cdot n_S + e_{ns}^t \cdot n_S - \frac{n}{\tau} \end{aligned} \quad (7)$$

For temperatures which are not too low, the optical excitation from the shallow level will give a minor contribution compared to the thermal excitation, so that second term in eq 6 and the third and fourth terms in eq 7 can be neglected. The difference in steady state electron concentration with and without I_1 can now be calculated from eqs 6 and 7.

$$\frac{\Delta n}{\tau} = \sigma(h\nu_1) \cdot I_1 \cdot (n_{T0} - \Delta n_T) + e_{ns}^t \Delta n_S + \sigma(h\nu_0) \cdot I_0 \cdot \Delta n_T \quad (8)$$

If $\frac{\Delta n}{n}$ is small, it follows that $\frac{\Delta n_S}{n_S} = \frac{\Delta n}{n}$

eg $\Delta n_S = K \cdot \Delta n$, which leads to $\Delta n(1+K) = -\Delta n_T$

If the intensity I_1 , is chosen so that $\sigma(h\nu_1) \cdot I_1 \ll \sigma(h\nu_0) \cdot I_0$

the small disturbance caused by I_1 does not effect the lifetime of the excess carriers and the relation between the optical cross-section (σ^0) and Δn can be derived from eq 8.

$$\sigma^0(h\nu_1) = \frac{\Delta n}{I_1} \cdot [1/\tau + \sigma^0(h\nu_0) \cdot I_0 \cdot (1+K) - e_{ns}^t \cdot K]/n_T \quad (9)$$

where all terms in the large bracket are assumed to be constant.

2. Experimental method

If the transient caused by I_1 is recorded and the difference in the steady photo-current measured, this would be a correct but not a sensitive method. To improve the signal-to-noise ratio, several transients could be recorded and averaged using a boxcar system with automatic baseline correction. Another way is to use a lock-in-amplifier and chop the I_1 light. If the light pulses are long compared to the effective time-constant, the signal from the lock-in-amplifier will be proportional to Δn and thus to $I_1 \cdot \sigma(h\nu_1)$, but independent of frequency. If, on the other hand, the time constant is long, a higher frequency could be used. The signal from the lock-in-amplifier will be

$$U = \frac{1}{T} \left(\int_{t_0}^{t_0+T/2} i(t) dt - \int_{t_0+T/2}^{t_0+T} i(t) dt \right)$$

and thus the maximum signal will be received with a phase shift of 90° relative to the chopper. In this case, it is obvious that the signal is not proportional to $I_1 \cdot \sigma(h\nu_1)$, but to $I_1 \cdot \sigma(h\nu_1)/f$, where f is the chopper frequency.

3. Material

To illustrate our measuring technique, measurements were performed at 300 K with a sample of high ohmic GaP. Ohmic contacts were made by alloying Zn dots on to the sample. The electric field in the sample was less than 100 V/cm. For the measurements, only photon energies smaller than half the band-gap were used, thus causing a homogeneous excitation in the samples. Hence, no spatial variation of the excitation density has to be considered. The high intensity light source used was a Reuter lamp with an interference filter at $1.18 \mu\text{m}$. A double monochromator (Zeiss MM 12) was used for the variable photon energy and the photocurrent was measured with a PAR 186 and a current amplifier PAR 181. No change in signal amplitude was observed using 4.5 Hz, 9.3 Hz and 17 Hz. The obtained photoionization cross sections are given in Fig 1 together with result of measurements using the constant photo-current technique ⁵⁾.

4. Quenching of photocurrent

Photoconductivity measurements in n-type material cannot only be used to investigate the spectral distribution of photoionization cross-section σ_n^0 of electrons. By applying a small

variation of the measuring technique, it is easily shown that the spectral distribution of photo-ionization cross-section σ_p^0 for the excitation of holes from the energy levels to the valence band can be measured for hole-capturing energy levels. The sample is first illuminated with a light source of high intensity I_s and constant photon energy $h\nu_s$ such that two-step excitation occurs. Due to this illumination, holes are created in the valence band and are the partially captured by hole traps. The rate of recombination will decrease and the photocurrent therefore increases. Simultaneously, electrons may be excited from the valence band into the hole-capturing impurity level. However, this level will not be filled with electrons because the hole occupancy P_T of these levels is for $h\nu_s < E_C - E_T$ given by

$$P_T = \frac{c_p^p}{c_p^p + c_n^n + e_{ps}} N_T$$

If the sample then simultaneously is illuminated also with photons of energy $E_C - E_T > h\nu > E_T - E_V$ which are able to release holes from the hole-capturing impurity level to the valence band, the rate of recombination will increase and thus the photocurrent will decrease. If this decrease (or quenching) of the photocurrent is small compared to the total current the quenching depends solely on the rate $e_p^0 p_T$ of the additional excitation of holes from the impurity level into the valence band due to photons of energy $h\nu$.

If this light is chopped at a suitable frequency, a similar lock-in method can be used. The a-c signal should either be independent of frequency or linearly dependent on frequency. The signal should also be linearly dependent on intensity $I(h\nu)$. To illustrate this experimental technique, results of the quenching of photoconductivity in a n-type GaP:Cu photoconductor are shown in Fig 2. For comparison, the same sample was investigated using the constant-quenching technique⁵⁾. In both cases, the high intensity light source was a Reuter lamp with an interference filter at 605 nm (2.05 eV).

Discussion

The advantage of the lock-in-amplifier method compared with that of constant current⁵⁾ is to be found in the principal difference between a measuring apparatus and a servo-system. A servo-system must detect or measure an error signal and then regulate to minimize it. A measuring equipment just measures "error signal" and registers it. From available data or suitable instruments, it is possible to estimate the detection limits of a lock-in-amplifier system in different cases. The most suitable photo-conducting sample to be measured by an electrometer is one with a dark resistance of $10^9 \Omega$ or more.

Using a chopper frequency of some hertz a system of PAR 186 lock-in-amplifier and a PAR 181 current amplifier an equivalent noise bandwidth of 1/32 Hz can be

obtained, due to the 18 dB per octave roll-off and a 3s time constant. From a noise figure table, it follows that the noise as referred to the input will be about 10^{-15} A if a voltage of 1V across the sample is used. This shows that although the experimental situation was chosen to suit the electrometer system, the lock-in-amplifier system will be superior to most electrometer systems. If, on the other hand, a low ohmic sample of 1 k Ω is chosen and the same lock-in-amplifier system used, the equivalent noise referred to the input is about 10^{-12} A if a voltage across the sample of 0.5 V is used. A similar sensitivity can scarcely be obtained using an electrometer system.

Concluding remarks

An analysis of a method using photocurrent for the determination of photo ionization cross section of impurity centers in semiconductors has been given. It is shown that the results obtained by this method are in agreement with those obtained by the constant photocurrent method ⁵⁾. The method presented extends the possibilities of performing photocurrent measurements to low ohmic samples.

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Figure captions

Fig 1 Spectral dependence of the photoionization cross section. The open circles are obtained from measurements according to ref 5 and the full circles from measurements according to the lock-in-method.

Fig 2 Spectral dependence of the photoionization cross section of GaP:Cu (Level A) at 300 K. The open and the full circles are obtained from measurements of constant quenching of photocurrent according to ref 5 and of the lock-in-method respectively.

